Hygroscopic Characteristics of Space Shuttle Tiles

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16. Abstract

The wettability of silane treated and untreated Space Shuttle tile was determined by measuring the rate of capillary rise of water through columnar pieces about 4 inches high. Application of the Washburn equation for the capillarity of porous materials gives the effective contact angle of the silica fibers themselves. This technique was used to show that the tiles can be made hydrophobic and non-wetting if the fibers are dehydroxylated by heating above 700°C in a vacuum chamber.

Various inorganic materials such as refractory metals, oxides, carbides and nitrides that might be applied to the fibers as antiwetting agents by chemical vapor deposition(CVD) after the tiles are fabricated have been investigated.

Amorphous SiC:H, made by plasma-activated CVD on Al foil, was found to be non-wetting for C/Si ratios greater than 1. The contact angle was unchanged after heating in air to 400°C.

These preliminary indications that it may be possible to waterproof TPS materials with CVD coatings of SiC:H should be followed up with more extensive studies to establish methods of applying such coatings to silica fibers and other materials.

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I SUMMARY

The tendency of untreated Space Shuttle tiles to absorb up to six times their own weight of water is related to the hydrophilic character of the surfaces of the amorphous silica fibers and the very porous structure (packing density only 6 percent) of this unusual heat shielding material. Current practice is to produce a water-repellent surface by attaching silane molecules to the surface hydrogens of the hydroxyl groups on the fiber surface although the protection is lost during reentry as the organic coating is burned off by the heat that is generated.

The wettability of treated and untreated Space Shuttle tile was determined by measuring the rate of capillary rise of water through columnar pieces about 4 inches high. Application of the Washburn equation for the capillarity of porous materials gives the effective contact angle of the silica fibers themselves. This technique was used to show that the tiles can be made hydrophobic and non-wetting if the fibers are dehydroxylated by heating above 700°C in a vacuum chamber. However the hydroxylated, i.e. hydrophilic, state is restored rapidly by exposure to water vapour at elevated temperatures or by wetting with alcohol.

Various inorganic materials such as refractory metals, oxides, carbides and nitrides that might be applied to the fibers as antiwetting agents by chemical vapour deposition or liquid infiltration after the tiles were fabricated have been investigated. Contact angle measurements were made using the tilting table technique on flat surfaces of bulk samples or as deposited on glass slides. No conventional chemical compound, including SiC, compatible with the various requirements for Space Shuttle tile materials exhibited a contact angle high enough to be considered water repellent after heating in air to 400°C.

Amorphous SiC:H, made by plasma-activated CVD (chemical vapour deposition) on Al foil, was found to be non-wetting for C/Si ratios greater than 1. The contact angle was unchanged after heating in air to 400°C. A sample of Space Shuttle tile with a CVD coating of crystalline SiC on its outer surface was found to be quite hygroscopic, i.e. absorbed water readily. Scanning electron micro-scopy showed that the coated surface was very porous as most fibers were coated uniformly with the SiC although some tendency for crystal growth to fill in the interstices of the tile structure was evident.

These preliminary indications that it may be possible to waterproof TPS materials with CVD coatings of SiC:H should be followed up with more extensive studies to establish methods of applying such coatings to silica fibers and other materials. Further basic research on the fundamental factors that affect wetting of inorganic materials is needed to develop the capacity to predict the wettability of a particular surface structure and composition.

II INTRODUCTION

The primary incentives to undertake basic studies of the wetting and waterproofing of Space Shuttle tiles, fabricated from highly hygroscopic silica fibers, are that the original waterproofing treatment applied at the factory is partially lost during reentry and post-mission treatments to restore waterproofing are required. Problems with discoloration of tiles by Scotchgard add to the interest in developing a more thermally-stable treatment that can be applied at the factory and will endure multiple missions.

Better understanding of the factors that affect the hygroscopic characteristics of Space Shuttle tiles may lead to new waterproofing materials and application methods. Further discussions of the background to the water absorption problem and of the wettability of silica are presented below.

Background To The Problem

The Thermal Protection System (TPS) for the Space Shuttle utilizes about 40,000 individual ceramic (high-purity silica and alumina borosilicate) fibrous "tiles" that are waterproofed by impregnating them at the factory with e.g. methyl-silane (like Dow Corning Z-6070) prior to adhesive bonding with RTV to the shell of the spacecraft. Waterproofing is essential as the otherwise highly hygroscopic (water absorbing) porous silica tiles could become saturated by exposure to rain adding considerable weight to the Space craft and the risk of damage due to freezing in flight. The outer surface of most tiles is coated with about 15 mils of Reaction Cured Glass (RCG = Vycor/B_2O_3 /SiB_4) (III-5,7)) to provide a black, high emissivity, coating. Although this coating is water-repellent, it is quite brittle and susceptible to damage from impacts by hard objects. Breaks in the RCG allow water to penetrate into tiles that were not otherwise waterproofed.

Waterproofing by injecting silane is effective but costly as the outer layer of the original silane coating is decomposed by heating during re-entry and must be renewed. In addition to the material and labor costs, recoating after each mission is disruptive to launch schedules because of the time required to dry a wet Spacecraft and the precautions that are necessary in handling rewaterproofing chemicals.

Estimates of Potential Water Entrapment

In order to fufill their design function to provide effective thermal protection during re-entry of the Space Shuttle and to minimize the weight of the TPS, the fibrous tiles are fabricated to a packing density of only 6 percent and hence are about 94 percent open space. Thus an uncoated 6x6x4 inch tile has the capacity to hold about 4.5 lbs. of water and laboratory measurements have verified that this estimate does indeed take place.

Present waterproofing can withstand re-entry temperatures to about one inch below the surface which limits water absorption to this outer portion of the tile. Even for this amount of water penetration, 40,000 saturated tiles could theoretically add "9 tons" to the weight of the space craft. Water loads of over one thousand pounds have been detected using Scotchguard and the circumstances where even more water could have been absorbed have been recognized. Water loads of this magnitude will reduce the available payload considerably and could lead to severe tile damage.

Thus the need to take considerable precautions to limit water pick-up to a tiny fraction of the available "capacity" and the desirability of a permanent waterproofing method are quite clear.

Factors Affecting Wetting Of Silica

Clean vitreous silica is quite hydrophilic and so the open fibrous structure of untreated Space Shuttle tiles makes them very hygroscopic due to capillary action. The value of the contact angle between a liquid and a solid surface is generally used as a "figure of merit" to indicate the extent of wetting to be expected. Materials with contact angles near 0 are hydrophilic and those with angles of 90 degrees are hydrophobic.

Although the wetting or non-wetting of glass, silica, and other materials is thought to be reasonably well understood, there are many apparent discrepancies in the extensive literature on hydrophylic-hydrophobic behavior of materials. A classic case is wetting of gold by water. It is only recently that it has been established that a clean gold surface is hydrophylic with a contact angle of 0 - 5 degrees. Unless great care is taken, the exposed surface becomes hydrophobic within a matter of minutes with a corresponding increase in contact angle to 50 - 80 degrees. This behaviour is due to contamination of the surface, usually with oil or other organic vapors present in ambient air, or by the formation of a chemisorbed oxygen layer if a "clean" atmosphere is maintained. No doubt many reports of non-wetting surfaces result from inadvertent and unsuspected deposition of airborne hydro- phobic contamination.

In the case of amorphous and crystalline silica and silicate glass, the pronounced hygroscopic behavior is a consequence of the occurence of surface silonal (SiOH) groups which are the primary sites for water absorption. A fully hydroxylated surface has about 4.6 silonal groups per square nanometer, i.e. with an average spacing of about 5 angstroms, however about one half of the silonals are in hydrogen-bonded pairs and the remainder are in the form of isolated silonals.

Water molecules cling to the surface silonals as their influence extends through several layers of water. The bound water is removed by heating to 150-175°C and the surface hydroxyls begin to come off during heating in vacuum to above 400°C. By 1000°C, the silonal concentration is reduced to 0.2 per nm^2. The silonal concentration recovers very rapidly during cooling in air at temperatures around 500-600°C. However, surface silonals can also be removed by heating in Cl gas or $SiCl_4$ at approximately 400°C. Any internal silonal groups that are trapped in micropores on the surface during the first stages of the production of silica fibers for the Space Shuttle tiles likely migrate to the surface during subsequent high temperature heating. However this opinion must be confirmed by infra-red spectroscopy.

III RESEARCH APPROACH AND OBJECTIVES

The initial approach to this program was to examine, conceptually and experimentally, the fundamental factors affecting water pick-up and retention by Space Shuttle tiles. Another intention was to explore novel methods of waterproofing to supplement or replace the current application of silane coatings that must be renewed after every mission. The third purpose was to identify a method of determining the moisture content of thermal protection tiles in place on the Space Shuttle.

These general considerations evolved into the following objectives and plans;

* Investigate the water absorption characteristics of treated and untreated samples of Space Shuttle tile.

* Consider their wetting behaviour in terms of contact angles and the hydrophillic character of silica surfaces.

* Determine the contact angles and thermal stability of inorganic materials that might be used to waterproof silica fibers.

* Consider methods of reducing the rate of water absorption as an alternate method of waterproofing.

* Try to coat the silica fibers in tile samples with a material that has a contact angle approaching 90 degrees or more. Coating fibers in tiles to a depth of about 1 cm. might be sufficient to effect adequate protection against unacceptable amounts of water absorption.

* Develop recommendations for the design of a portable moisture meter for field surveys on the Space Shuttle.

As the work progressed, additional contact angle measurements, characterization studies and conceptual analyses were carried out to enhance efforts to uncover new approaches to waterproofing ceramic materials. The primary add-on activities were; (1) the use of NMR to determine surface hydroxyl concentrations, (2) measurement of the contact angles of amorphous CVD films of SiC:H, (3) SEM examination of CVD SiC coatings and (4) correlating the contact angles of materials with their dielectric properties.

IV EXPERIMENTAL RESULTS

The experimental findings are reviewed in the general order of the objectives listed in Section III.

a) Wetting Of Space Shuttle Tile Samples

As discussed above, the wetting tendancy of materials is commonly described in terms of their contact angles with the fluid in question. The effective contact angle of porous media such as Space Shuttle tiles can be determined in several ways. The most straight forward is to measure the height of capillary rise and relate this to the contact angle by mathematical relationships involving fiber size, shape and orientation and the tile pore volume. An estimate of the height of capillary rise based on this relationsnip was included in the original research proposal. The result, illustrated in Figure 1, showed that the height would be as much as one half a meter, far beyond the dimensions of any samples that could be taken from representative pieces of Space Shuttle tile. Thus a simple capillary height measurement in this case is out of the question because of the extreme hydrophilic nature of uncoated silica fibers. On the other hand the coated fibers are completely waterproofed and the capillary rise would be 0 (or negative) and the contact angle cannot be determined with this technique.

The alternate approach is to observe the _rate_ of capillary rise by measuring the height of the water column in a square pyramid of tile as a function of time and apply the well-known Washburn equation. The experimental arrangement and the applicable Washburn equation are illustrated in Figure 2. The equation includes a tortuosity factor (K) which also involves the size, shape and volume fraction of the fibers in tne tile. It is possible to make a reasonable estimate of the K factor but it is convenient to leave it as an unknown, but constant, parameter (IV-B-5,6).

A large number of measurements were made of the rate of rise of water in specimens that were typically about 1 cm square at the base and 6-8 cm. long as illustrated schematically in Figure 3. Small marks were put on the cylinder to aid in observing the height of the column at a particular time. Typical times for the water to reach the top were in the order of 30 seconds and it was not difficult to note the passage of each of the marks within a second or two. Typical plots of the square of the water column height against time are shown in Figure 4. The slope of such plots is directly related to the contact angle of the porous matrix material, as well as the temperature of the water because of the variation of viscosity and surface tension with temperature. Similar plots are shown in Figure 5 along with corrections of the slope for viscosity to determine the selective values of K to the "tortuosity" factor.

It will be noted from the values shown for K that the correction for viscosity does not remove all of the temperature dependence (the correction for surface tension changes is quite small). A plot of K cos θ vs temperature, corrected for viscosity, for all of the data is shown in Figure 6. Despite the scatter and correction for viscosity a clear trend for a reduction in K cos θ with temperature is evident and is a crude measure of the "heat of wetting". The scatter, due to experimental variables such as the source and volume of distilled water, and other factors, was reduced as improved procedures were developed.

Rise-rate measurements were made on uncoated, as received, tile samples and those that had been waterproofed and after various processing techniques. The results are summarized as a bar graph in Figure 7. No capillary rise occurred in samples that had been waterproofed by the manufacturer and in fact the non-wetting of forcibly submerged, hydrophobic, specimens could be observed corresponding to a contact angle of 90° or more. It was commonly observed that the rapid rise rate (slope) in untreated samples declined with repeated testing. This effect may be due to some alterations of the fibrous structure, increasing the tortuosity, as some shrinkage (and hence densification) was noted, and a trace of a chalky residue was evident when the water in the petri dish evaporated. When alcohol was substituted for water the rise rate was more rapid presumably due to reduced viscosity.

Heating untreated, as-received tile samples in vacuum at 800°C or above made them hydrophobic as shown in Figure 7. It was important to cool the samples to room temperature in vacuum to achieve a hydrophobic condition that would persist during storage in a dessicator for many weeks. However, essentially normal hydrophobic behavior resulted when rise measurements were made with alcohol or with water on samples that had been heated in H_2 or in air at 400°C.

Strips of flexible "quilt" made up of woven silica fibers were also mounted for rise rate measurements. As expected, the waterproofed material showed completely hydrophobic behavior whereas heating in air at 690°C for 1 hour destroyed the waterproofing. Because of differences in fiber diameter and the more open structure of the quilts, a direct comparison of K cos θ value is not appropriate. The heated quilt sample took up water quite readily.

b) Contact Angle Measurements On Candidate Coatings.

The compounds under consideration as inorganic water-proofing coatings for silica fibers were generally only available as relatively flat samples or after deposition on glass slides or some other planar material. Some initial experiments were carried out using a flat wedge arrangement as described in detail in UCB senior project report by Laura Powers (submitted previously). Although this method is quite sensitive in principle, in practice it was difficult to observe the height of the miniscus in the wedge-shaped capillary for many of the films that were opaque. Another problem was that CVD processes caused distortion of the glass slide so that the wedge-angle did not remain constant across the width or along the length of the slide.

A more conventional technique for measuring contact angles is the tilting table arrangement where the specimen is mounted on a goniometer and the angle that it makes with the surface of the water when the meniscus is flat can be measured quite accurately. This tilting table technique was used for the measurements that are reported in this report. The results are summarized in Table 1 for a variety of candidate and reference materials. These results are discussed in Section V.

c) Contact Angles Of CVD Films Of SiC:H.

Samples of plasma-activated CVD films of SiC:H deposited on Al foil were obtained from Prof. J.A. Reimer of the Chemical Engineering Dept. of UC Berkeley. The results of measurements of contact angles of CVD films of SiC:H with different silicon/carbon ratios are shown in Table II and plotted in Figure 8. It may be noted that the higher the carbon content, that is, the lower the silicon-carbon ratio, the higher the contact angle. Contact angles of this magnitude would be high enough to provide an effective level of water-proofing in Space Shuttle tiles. The results of other studies of SiC:H and the apparent reason for the dependence of contact angle on carbon content is discussed in Section V.

Specimens were also evaluated after they had been heated in air for 10 minutes at 400 C. This treatment does not simulate the reentry condition but the number of samples that were available were quite limited so that the plan was to gradually increase the exposure to to evaluate the thermal stability. The measurements showed that heating to this temperature had no effect on contact angle whereas this is not the case for crystalline SiC. Bulk silicon-carbide, for example, oxidizes sufficiently to drop the contact angle down to that of vitreous silica. (Subsequent tests by J.A. Reimer revealed that heating to 600°C causes the SiC:H films to break up and spall from the glass so that it was not possible to determine a contact angle.)

d) Electron Microscope Examination Of A CVD Coating Of SiC On Space Shuttle Tile Fibers.

Scanning electron microscopy was used in the preliminary work to observe the fibrous structure of Space Shuttle tiles. Micrographs showing the fibers with and without silane water-proofing were included in the report by Laura Powers. Of particular interest is the observation that the Scotchguard coating need not cover the entire fiber surface to achieve an apparent fully effective waterproofing. Quantitative studies of this observation would be valuable.

For comparison with the amorphous CVD SiC:H films, samples of the CVD coated with crystalline SiC were supplied by the Technical Monitor for SEM examination. Representative micrographs are shown in Figures 9 and 10. As is evident from the micrographs of the surface and interior structure, the CVD coating does not penetrate into the tile beyond a fraction of a millimeter, nor does it form the solid coating that would be required to provide a waterproof coating for the entire tile. Experiments confirmed that the sample was quite hygroscopic.

e) NMR Measurements of Hydroxyl Content Of Fibers.

Nuclear magnetic resonance is a powerful technique for measuring the hydrogen content (in this case, OH content) of the silica fibers. Several samples were measured, courtesy of Mark Petrich, in the Chemical Engineering Dept. at the University of California. Samples of 4 tiles with different thermal histories were crushed and about 50 milligrams of powder were tamped into quartz vials and sealed. One sample was "as received" (i.e. no waterproofing or other treatment), two others had been heated in vacuum to 800°C and 1000°C to remove the surface hydroxyls and the fourth had been rinsed to restore the water content after vacuum dehydration.

The NMR curves are given in Fig. 11 and H contents derived from the data are presented in Table III. The variation between the samples is smaller than was originally expected from simple calculations of the effects of removal of the surface hydroxyls from the fiber. It is possible that crushing and tamping the fiber into the vial resulted in a significant level of moisture pick-up.

On face value, the interpretation of these results is that the internal hydroxyl content of the fibers is fairly significant amounting to several hundred parts per million. The surface hydroxyls are removed during the vacuum drying treatment resulting in a decrease in NMR signal. Surface hydroxyls are restored when the sample is immersed in water so that the hydrogen content increases again. However, as stated above, the variation is less than anticipated and these measurements should be repeated. Nevertheless this preliminary work shows that NMR does have the sensitivity to measure the OH content as predicted and in principle is a very powerful method of monitoring the amount of water adsorbed on the surface as well as the hydroxyl content at the surface and in the interior of the fibers.

V DISCUSSION AND CONCLUSIONS

As discussed previously, this project was intended to be an exploratory study of the feasibility of developing an inorganic non-wetting coating on the surface of the silica fibers, used in Space Shuttle Thermal Protection System that exhibit greater thermal stability than the fluorocarbon compounds that are commonly used. Even if such a compound could be discovered (the "classical" surface science view of wettability leads to a very pessimistic opinion on the chances of success) it would not be of practical use for the Space Shuttle if it degraded the properties of the fibers or would not adhere well to them. Ideally it should be possible to coat fibers within the finished block rather than as individual fibers. The results of this work indicate that there is a good chance that a new class of waterproofing materials can be developed and a reasonable chance that they would be applicable to Space Shuttle Thermal Protection Systems.

The primary results, observations and considerations are as follows;

1) The contact angles of fibers in heat shield materials can be determined by quantitative measurements of rate of capillary rise and application of the Washburn equation.

2) Contact angles of 5 - 10 degrees (similar to highly wetting fused silica and glass) observed on uncoated samples.

3) Contact angles > 90 degrees observed on samples treated with Scotchguard.

4) Removal of hydroxyls (OH) by vacuum drying (>800°C) produces a hydrophobic surface.

5) Hydrophobicity lost by heating in air or tank hydrogen (>400°C) or rinsing with acid or alcohol.

6) Prior removal of surface hydroxyls may be necessary to achieve good adherence of hydrophobic coatings.

7) Contact angles of potential coatings deposited on glass or aluminum and flat samples of reference materials measured using the tilting table method.

8) CVD films of amorphous "TiN" or "SiC:H" on glass are non-wetting.

9) SiC:H remains hydrophobic after heating to 400°C whereas TiN or bulk SiC do not (however, SiC"H films disintegrate when heated to 600°C).

10) Preliminary attempts to apply CVD coatings to fibers within a tile were not successful (subsurface penetration limited to a few micrometers).

11) Correlation between contact angle and dielectric constant provides a useful guide to identifying potential compounds for application as waterproofing coatings.

12) NMR instrumentation can be used for field inspection of wet tiles. (Specific design criteria could be developed.)

VI RECOMMENDATIONS FOR FURTHER WORK

The results of this project suggest that it should be possible to develop new methods of waterproofing Space Shuttle tiles and other materials. However, in as much as this project was primarily an exploratory study of the feasibility of developing an inorganic waterproofing material, it was not possible to follow up many of the observations or measurements to the extent needed to establish a practical process or that is desirable for publication. It should be noted in this respect that untreated Space Shuttle tile, comprised of relatively uniform fine fibers of pure silica, is an ideal material for basic studies of the hydroxyl structure and as well as other surface properties.

Further work should be carried out in several areas as discussed below.

Modelling of Capillary Rise in Fibrous Materials

The wettability of samples of Space Shuttle tile was deduced from the rate of capillary rise of water. The rate data was interpreted using the Washburn equation to obtain an "effective" contact angle that includes a tortuosity factor (k) that depends on fiber size and orientation. Extension of the Washburn equation to include the range of fiber diameters and non-random orientations that exist in real rather than hypothetical silica fiber structures (such as in heat shield blankets) would allow for a more quantitative interpretation of the data already available. Another valuable and necessary modification of the available model for capillary rise in fibrous materials is for cases where several kinds of particles or fibers with different contact angles are present in the tile or fabric.

Characterization of Surface Hydroxyl Concentration

The highly hygroscopic nature of untreated silica surfaces is due to the presence of a high concentration of hydroxyl groups. The removal of most or all of these groups by heating to 800-1000°C in a vacuum resulted in a temporarily hydrophobic surface. Current knowledge and understanding of the structure and concentration of surface silonals is based on work with fine silica gel particles carried out several years ago. The high purity, fibrous silica Thermal Protection Systems material is ideal for further studies employing modern instrumentation and interpretive models.

The most useful techniques are high field Nuclear Magnetic Resonance, Infrared and near infrared Spectroscopy to determine surface hydroxyl concentrations before and after thermal processing and wetting.

Extent Contact Angle Measurements on CVD SiC:H

Previous studies showed that CVD coatings on flat substrates of SiC:H with a C/Si ratio > 1 exhibit rather high contact angles and maintain their water-repellent nature after heating in air to 400°C.

More films of this type should be prepared and the limits of thermal stability established. In addition to measuring contact angles, the dielectric constants of the films should be determined.

Determine the Wettability of CVD Crystalline Diamond Films

The theoretical basis for predicting contact angles, i.e. wettability, of materials from their dielectric constants must be analyzed in greater detail. The most important consideration will be to examine the polarizability of surfaces for cases such as silica where the bulk dielectric constant does not apply because of the presence of highly polarizable hydroxyl groups at the surface.

Examine the Theoretical Basis for the Dependence of Contact Angle on Dielectric Constant

A strong correlation between the contact angle with water of a particular material and its dielectric constant (and the closely related index of refraction) has been noticed. Such a relation is plausible since the magnitude of Van der Waals binding is related to the polarizability of the material. Furthermore, a rather similar approach has been used to interpret the dispersion of powders in terms of the polarizability of the suspending liquid.

The correlation that was demonstrated (possibly for the first time) was largely based on contact angles and dielectric constants published in handbooks. These data relate to similar but not identical samples. Because of the theoretical importance and predictive value of a quantitative model, some new, more reliable measurements of contact angle and dielectric constant on identical samples are needed.

Explore Methods of CVD Coating of Fibers Within a Bulk Sample

The initial efforts to effect subsurface CVD on samples of Space Shuttle were not successful. New approaches to obtain useful penetration of this very promising material should be undertaken.

Infiltration with Water Repellent Powders

The waterproofing effects and feasibility of infiltrating the surface of TPS materials with hydrophobic powders such as carbon black, teflon and other fluorocarbon solids should be explored. In addition to being water-repellent, not cause deterioration of the silica fiber and be of a suitable size for infiltration, the ideal powder should have a self-restoring character so that the effects of re-entry will maintain or restore its hydrophobic surface. The effectiveness of various waterproofing particulates could be determined using capillary rise measurements and the extended Washburn equation outlined above.

Infiltration of Solgel Coatings

Infiltration of TPS materials with solutions that would leave a non-wetting coating when drained from the TPS tile and dried is a plausible approach to overcoming problems with achieving internal CVD coatings. Vacuum or triple-point drying may be required to produce a very thin but non-wetting surface layer. Both organic and non-organic solgel methods of depositions could be explored.

Acknowledgements

BIBLIOGRAPHY

The literature on scientific and technological topics relevant to
the wetting of silica and waterproofing of Space Shuttle Tiles is
very extensive.   Several hundred articles were examined and many
were copied.   Close contact between LBL-CAM and NASA-AMES through
Dr. Robert Altman included provision of information pertaining to
the production of components and characteristics of the Space
Shuttle Thermal Protection System and waterproofing methods from
NASA contractor reports and other pertinant information not
readily avaiable at UC Berkeley or the Lawrence Berkeley Lab.

References of particular value to someone initiating research on
this subject are listed below.

Selected References

I. Production and Properties of Space Shuttle Tiles

1) Cooper, Paul A., and Paul F. Holloway, "The Shuttle Tile Story",
   Astronautics and Aeronautics, Jan 1981, 19[1] pp. 24-34.

2) Dotts, R.L., et al., "Moisture Absorption Characteristics of the
   Orbiter Thermal Protection System and Methods Used to Prevent
   Water Ingestion", SAE paper # 831117.

3) Dotts, R.L., et al., "The Shuttle Orbiter Thermal Protection System
   Materials, Designs, and Flight Performance Overview", SAE paper #
   831118.

4) Goldstein, H., "Fibrous Ceramic Insulation" (Ames Research Center)
   Presented at NASA/AIAA Advanced Materials Technology Conference,
   Nov. 16-17, 1982

5) Green, D.J., J.E. Ritter and F.F. Lange, "Fracture Behavior of Low
   Density Fibrous Ceramics",Journal of the American Ceramic Society,
   March 1982, 65[3] pp.141-146.

6) Holt, J.W., and L.W. Smiser, "Surface Densification of High-Porosity
   Silica Insulation", SAMPE Quarterly, July 1981, 12[4] pp. 14-18.

7) Korb, L.J., and H.M. Clancy, "Shuttle Orbiter Thermal Protection
   System; A Material and Structural Overview", Rockwell International
   Paper STS 81-0219, Presented at the 26th National Symposium of the
   Society for the Advancement of Material and Process Engineering,
   4/28-30/1981.

8) Wehrenberg, R.H., "Exotic Heat-Resistant Materials Bring Back The
   Shuttle", Materials Engineering, Jan/June 1981, 93[3] pp. 60-62.

II. Waterproofing of Space Shuttle Tiles

1) "Rewaterproofing Silica Tiles", Nasa Tech Briefs, Spring 1983, 7[3] pp. 345-346.

2) "Waterproofing Agents for Silica Tiles", Nasa Tech Briefs, Spring 1985, pp. 109-110.

3) "Keeping the Orbiters High and Dry", Rockwell International Co. Journal The Engineering Observer, June/July 1983, 7[8].

4) "A Study For An Improved High Temperature Waterproofing Compound For The Space Shuttle Orbiter Thermal Protection System", Third Monthly Progress Report of NASA Contract - NASIO-11116.

5) "Results of the AFRSI Rewaterproofing Systems Screening Tests" NASA CR 167694.

III. Basic Factors Affecting the Wetting of Silica, Ceramics, and Other Selected Materials

1) Adamson, Arthur, Physical Chemistry of Surfaces, 4th Ed. Wiley Interscience, New York, 1982.

2) Anderson, S., and D.D. Kimpton, "Some Phenomena Related to the Hydrophobicity of Silicate Glasses and Adsorbed Oxygen", Journal of the American Ceramic Society, Sept. 1960, 43[9] pp. 484-488.

3) Brooks, C.S., M.A. DeCrescente and D.A. Scola, "The Wetting of Silicon Carbide Surfaces", Journal of Colloid and Interface Science, Aug. 1968, 27[4] pp. 772-788.

4) Dettre, R.H. and R.E. Johnson, "Wettability and Contact Angles", in Surface and Colloid Sciece, Vol 2., Ed. by E. Matijevic, Wiley Interscience, New York, 1969.

5) Erb, Robert, "The Wettability of Gold", Journal of Physical Chemistry, July 1968, 72[7] pp. 2412-2417.

6) Fowkes, F.(editor), Hydrophobic Surfaces, Academic Press, 1969.

7) Gaines, G.L., "On the Water Wettability of Gold", Journal of Colloid and Interface Science, Jan. 1981, 79[1] p. 295.

8) Holland, L., The Properties of Glass Surfaces, John Wiley & Sons, New York, 1964, pp. 348-366.

9) Hubball, J.A., et al, "Preliminary Investigation of the Effects of Gamma-Radiation on the Surface of Raw Fused-Silica Tubing" Journal of Chromotography, 1984, v.302 pp341-350.

10) Iler, Ralph K., The Chemistry of Silica, John Wiley a Sons, New York, 1979. (esp. Chapters One and Six)

11) Laskowski, J., and J.A. Kitchener, "The Hydrophilic-Hydrophobic Transition on Silica",Journal of Colloid and Interface Sci. April 1969, 29[4] pp. 670-679.

12) Nishioka, G.A., and J.A. Schramke, "Thermodesorption of Water from Silicate Surfaces", Journal of Colloid and Interface Science, May 1985, 105[1] pp. 102-111.

13) Schneegans, M., and E. Menzel, "Gold Crystals Solidified in Air Are Hydrophilic", Journal of Colloid and Interface Science, July 1982, 88[1] pp. 97-99.

14) Schrader, Malcolm, "Ultrahigh-Vacuum Techniques in the Measurement of Contact Angles. II. Water on Gold.", Journal of Physical Chemistry, 1970, 74[11] pp. 2313-2317.

15) Schrader, Malcolm, "Ultrahigh-Vacuum Techniques in the Measurement of Contact Angles. IV. Water on Graphite (0001)." Journal of Physical Chemistry, 1975, 79[23] pp. 2508-2515.

16) Olsen, D., "The Critical Surface Tension of Glass", Journal of Physical Chemistry, Sept. 1964, 68[9] pp. 2730-2732.

17) Wade, W.H., and N. Hackerman, "Thermodynamics of Wetting of Solid Oxides", Contact Angle, Wettability, and Adhesion, Advances in Chemistry Series, No. 43, American Chemical Society, Washington D.C., 1964, pp.222-231.

18) Zisman, W.A., "Relation to the Equilibrium Contact Angle to Liquid and Solid Constituion", Contact Angle, Wettability, and Adhesion Advances in Chemistry Series, No. 43, American Chemical Society, Washington D.C., 1964, pp. 1-51.

19) Conway,B.E., "The State Of Water and Hydrated Ions At Interfaces", Advances In Colloid and Interface Science Vol. 8 (1977) 91-92.

IV Experimental Techniques

A) Contact angle measurements of powders and fibers

1) Levine, S., and G. Neale, "Theory of the Rate of Wetting of a Porous Medium", Journal Chem. Soc., Faraday Trans. 2, 1975, 7[1] pp. 12-21.

2) Levine, S., and G. Neale, "A Theory of the Rate of Wetting of A Finely Dispersed Random Porous Medium" in Wetting, Spreading and Adhesion, edited by J.F. Paddy, Academic Press, London, 1978.

3) Uhlmann, D., O.C. de Hodgins and M.S. Dresselhaus, "Contact Angle Measurements of Wetting in Pristine and Ion Implanted High Modulus Benzene Derived Graphite Fibers", Materials Res. Soc. Symp. Proc. Vol 40, Materials Science Research Society, 1985   pp. 110-116.

4) Williams, R., "The Capillary Without Walls", Journal of Colloid and Interface Science, Jan. 1981, 79[1] pp.287-288.

5) Washburn, E.W., "The Dynamics of Capillary Flow", Phys. Rev. 1921, 27 [3], pp. 273-80.

6) Following oral presentation of the results of this work at the April 1987 meeting of the Materials Research Society , (Appendix III), Dr. Stephen Chwastiak of the Sohio Engineered Materials Co., Niagara Falls, NY, informed the author that he had used a similar "wicking" technique to measure the wettability of carbon fibers: (J. of Colloid and Interface Science, 1974).

B) Determination of the hydroxyl concentration on the surface of silica

1) McDonald, R.S., "Surface Functionality of Amorphous Silica by Infrared Spectroscopy", Journal of Physical Chemistry, ct. 1958, 62[9] pp.1168-1178.

2) Van De Venne, J.L.M., Rindt, J.P.M., Coenen, G.J.M., "Characterization Of A Thermally And Chemically Modified Silica Surface By Infrared Spectroscopy Using The Mull Technique" J. of Colloid and Interface Science Vol.74, (1980) pp. 287-290.

V   Preparation And Properties of CVD Films

1) Fisher, R.M., Posthill, J.B., Sarikaya, M., Reimer, J.A. Petrich, M., "Electron Optical Characterization of Amorphous SiC:H Films" Mat. Res. Soc. Symp. V69, pp. 153-158.

2) Mahan, A.,H., von Roedern, B., Williamson, D.,L., Madean, A. "Amorphous Silicon Carbon Alloys" J. Appl. Phys., V 57 (1984) pp. 2717-2720.

TABLE I

CONTACT ANGLES WITH WATER

MATERIAL	PREPARATION	MEASURED VALUE-DEGREES
Glass slide	Alcohol Rinse	0 - 10
Fused Silica	" "	2 - 10
Stainless Steel	" "	25 - 35
" "	10 min. at 400 C in air	20 - 30
Chromium	Vapour-deposited	25 - 35
"	10 min. at 400 C in air	15 - 20
SiC (bulk)	polished and cleaned	40 - 50
"	10 min. at 400 C in air	15 - 25
Pyrolytic graphite	polished and cleaned	80 - 90
" "	10 min. at 400 C in air	80 - 90
Polyproplene	as-received	100 - 110
SCOTCHGUARD™ 733	sprayed on glass	>130
"TiN" (amorphous)	CVD on glass (576 C in $TiCl_4 + NH_4$)	60 - 70
"	10 min. at 400 C in air	30 - 40

TABLE II

CONTACT ANGLES WITH WATER

Experimental Amorphous Chemical Vapor Deposited Coatings

SAMPLE	PREPARATION	ANGLE - DEGREES
"Si:H"	Plasma CVD on Al foil (5% SiH_4 in He)	30 - 40 *
"	10 min. at 400 C in air	20 - 30
SiC:H (Si/C = 6/1)	Plasma CVD on Al foil (2% SiH_4 + 3% CH_4 in He)	60 - 70 *
"	10 min. at 400 C in air	" "
"SiC:H" (Si/C = 3/2)	Plasma CVD on Al foil (1% SiH_4 + 4% CH_4 in He)	80 - 90 *
"	10 min. at 400 C in air	80 - 90

* Note that the contact angle increases with increasing carbon content

TABLE III

NMR Studies of Space Shuttle Tiles

Sample	Wt % H	Ratio	Line Shape
o. 1 as received	0.031	1	Wide-Duplex
o. 2 1st vacuum treatment	0.021	.68	Wide
o. 3 2nd vacuum treatment	0.0165	.53	Wide
o. 4 after three soakings	0.0182	.59	Duplex

Interpretation – large H content within
silica fibers – partially
removed along with surface
–OH by vacuum treating
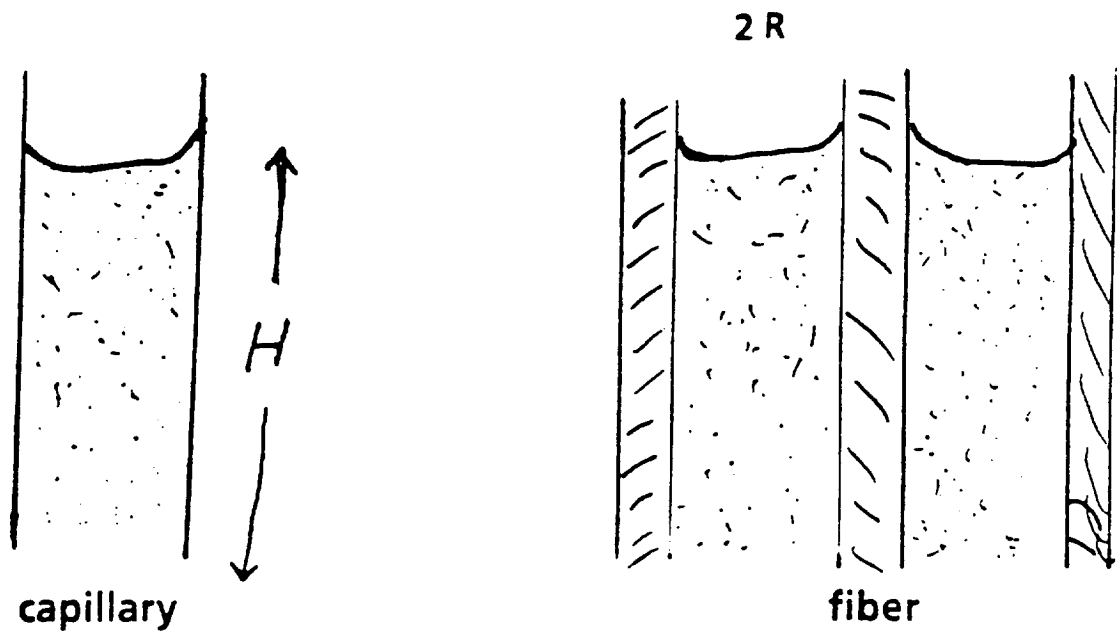
Space

$$H = \frac{2}{g} \left(\frac{\gamma}{\rho}\right) \frac{\cos \theta}{R}$$

for $\cos \theta \sim 1$

$R \quad \sim 10^{-4} \text{ cm}$

$H \quad \approx 45 \text{ cm}$

γ = surface tension
ρ = density
θ = contact angle

Fig. 1   Schematic illustration of capillary rise (wicking) in untreated Space Shuttle tiles.
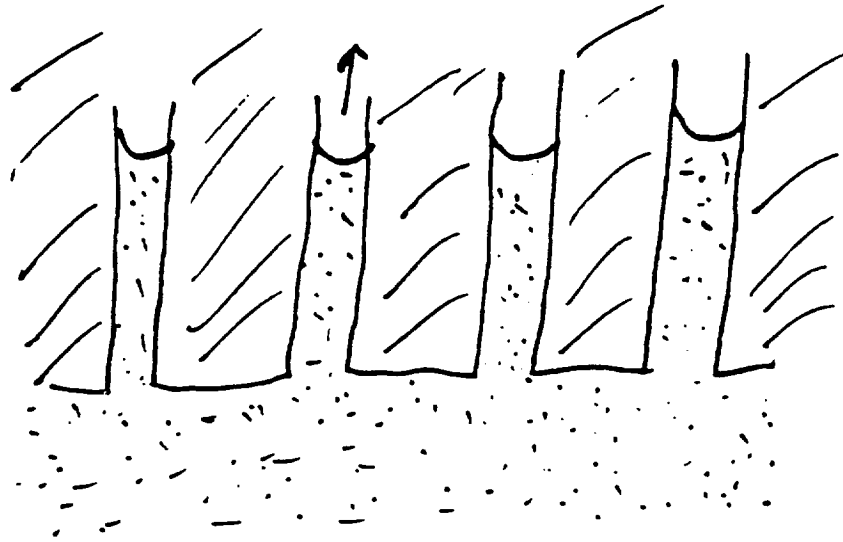
Rate of Penetration into Porous Media

$$\frac{dH}{dt} = \frac{1}{4}\left(\frac{\gamma}{n}\right)\frac{1}{H}\frac{(K)R}{}\cos\theta$$

$$H^2 = K\cos\theta \bullet t$$

γ surface tension

n viscosity

θ contact angle

t time

k "tortuosity" factor

R radius

Fig. 2   Schematic illustration of method of determining contact angle from the rate of "wicking" of Space Shuttle tile samples. The analytical expression is commonly known as the Washburn equation. The value of the tortuosity factor (k) depends on particle size and packing effects that add resistance to capillary flow.
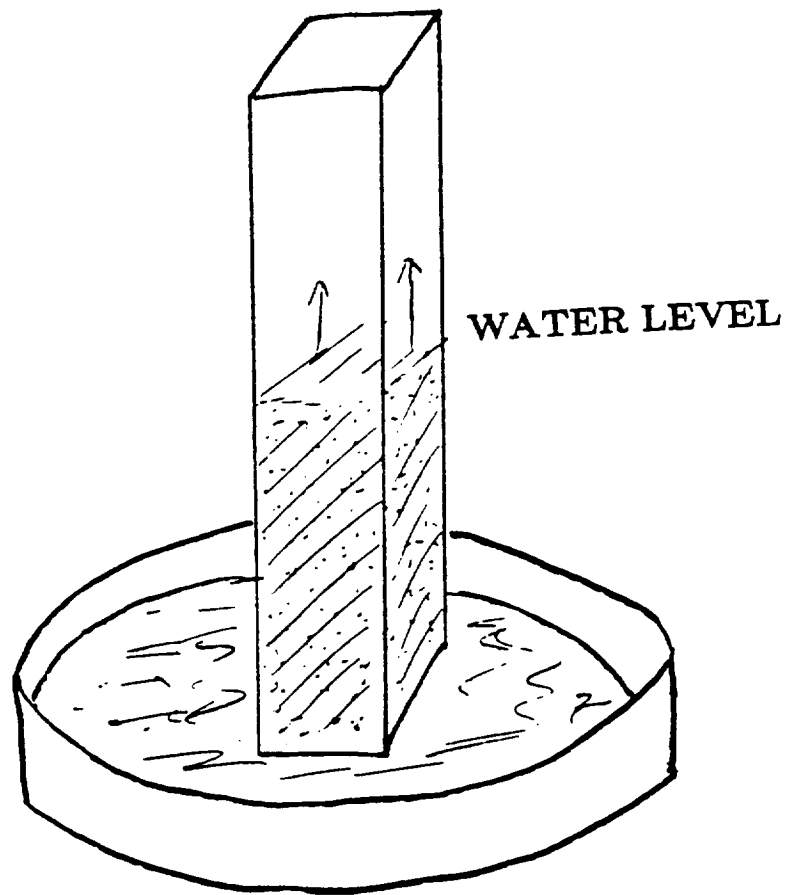
Fig. 3 Schematic illustration of water rise rate measurement arrangement.

Rate of Water Absorption in Space Shuttle Tiles
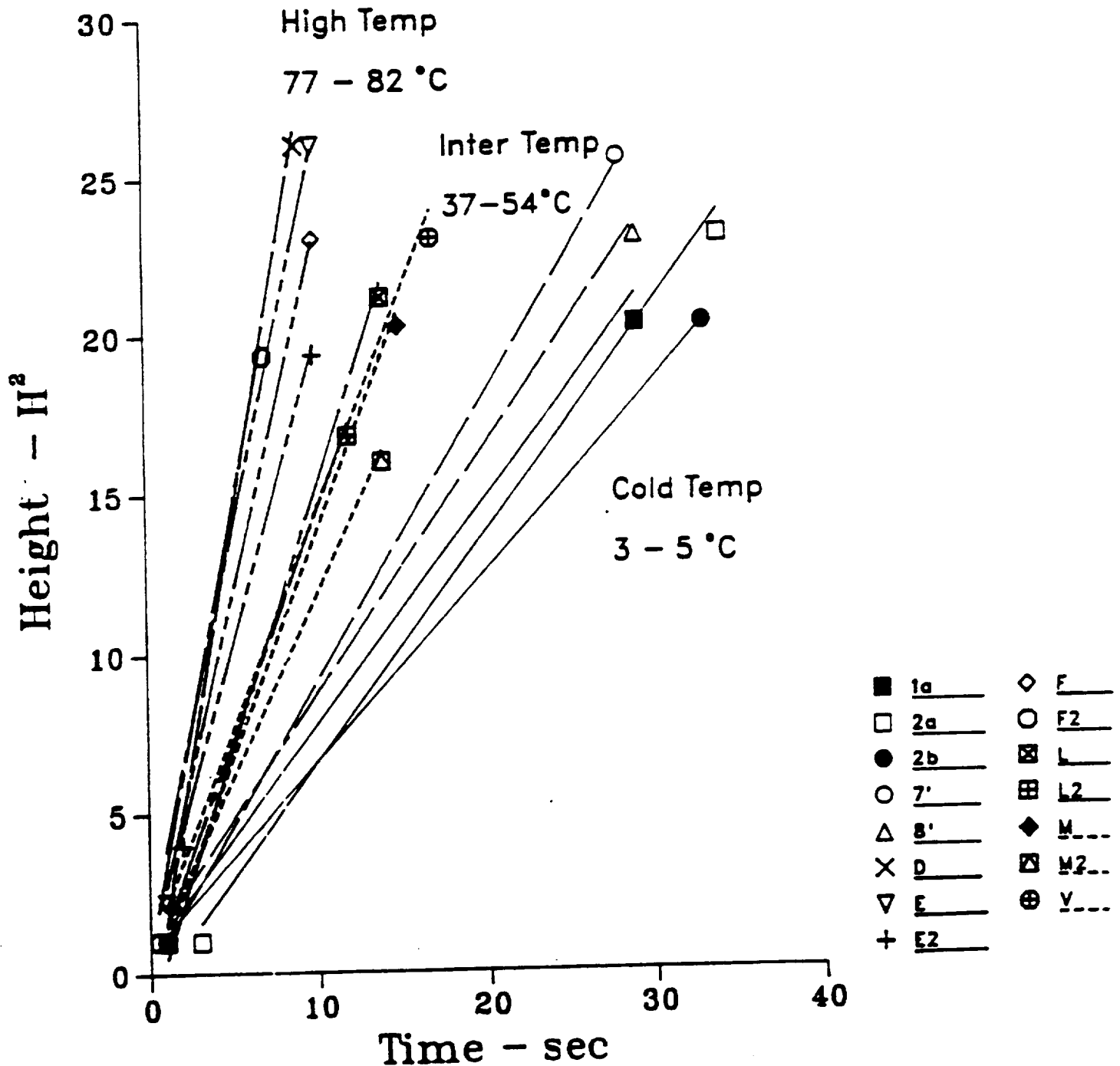
Fig. 4 Representative plots of results of water rise rate measurements at various temperatures.

Effect of Water Temperature on Rate of Absorption in Space Shuttle Tiles

H_2O @ 23°C
slope = .85
= 36K/η
= 36K/.0093
K = .220 x 10^{-3}

H_2O @ 2°C
slope = .59
= 36K/η
= 36K/.0167
K= .274 x 10^{-3}
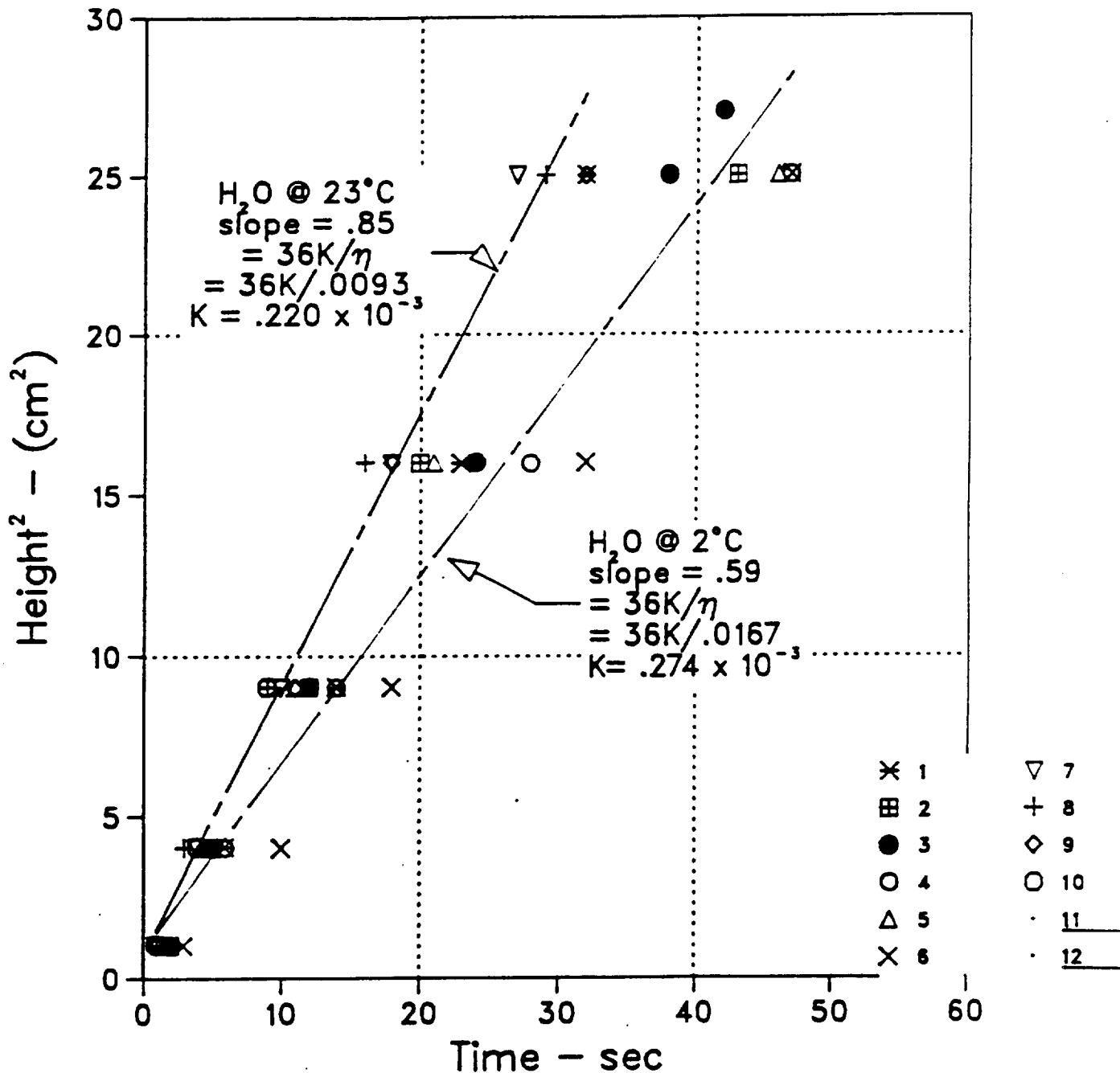
Fig. 5 Representative plots of rise rate measurements corrected for water viscosity. A smaller correction for the effect of temperature on surface tension was not made.
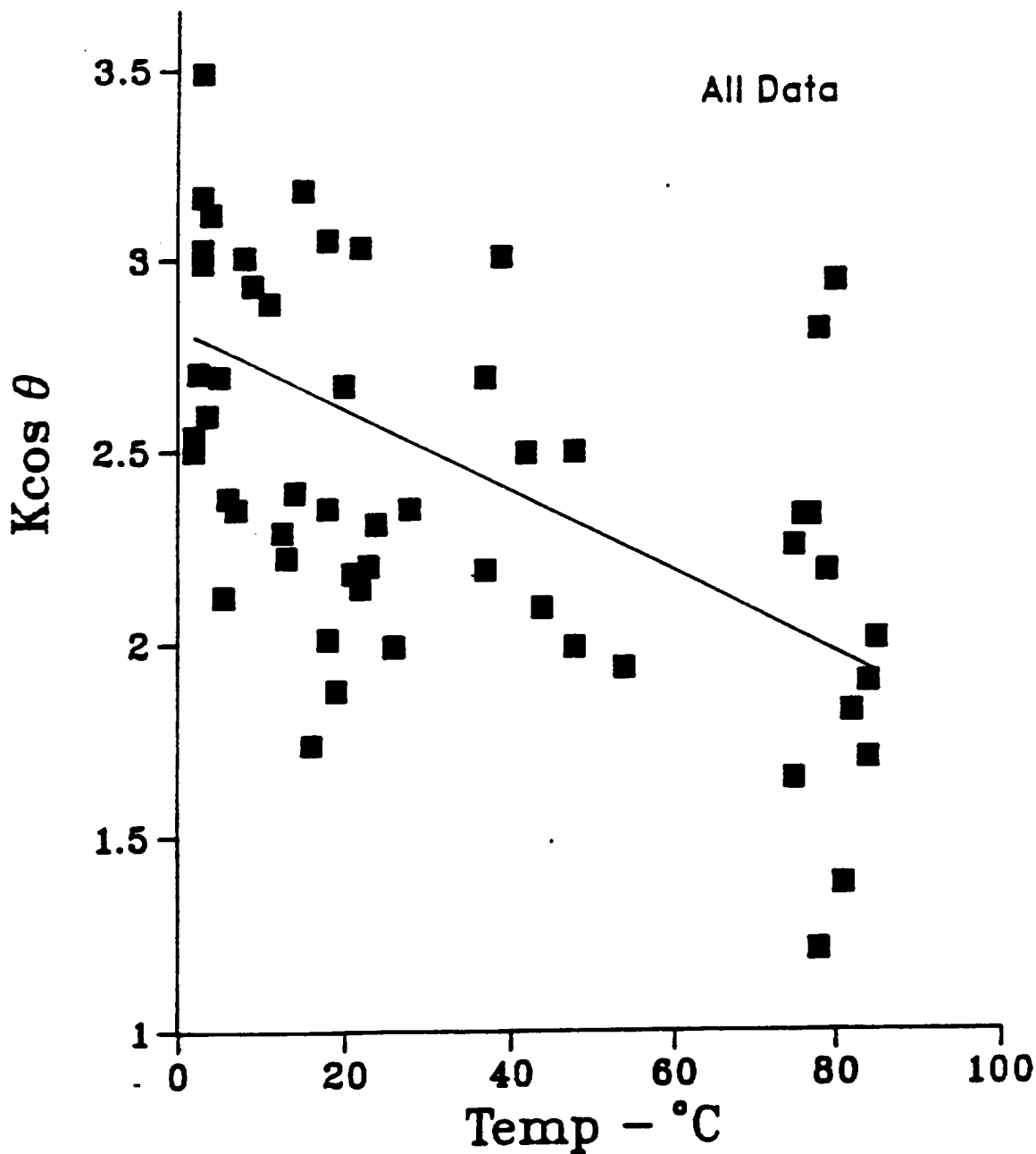
Fig. 6. Plot of all rise rate measurements illustrating effect of water temperature. (Correction made for viscosity but not surface tension.)

Water Absorption of Space Shuttle Heat Shields
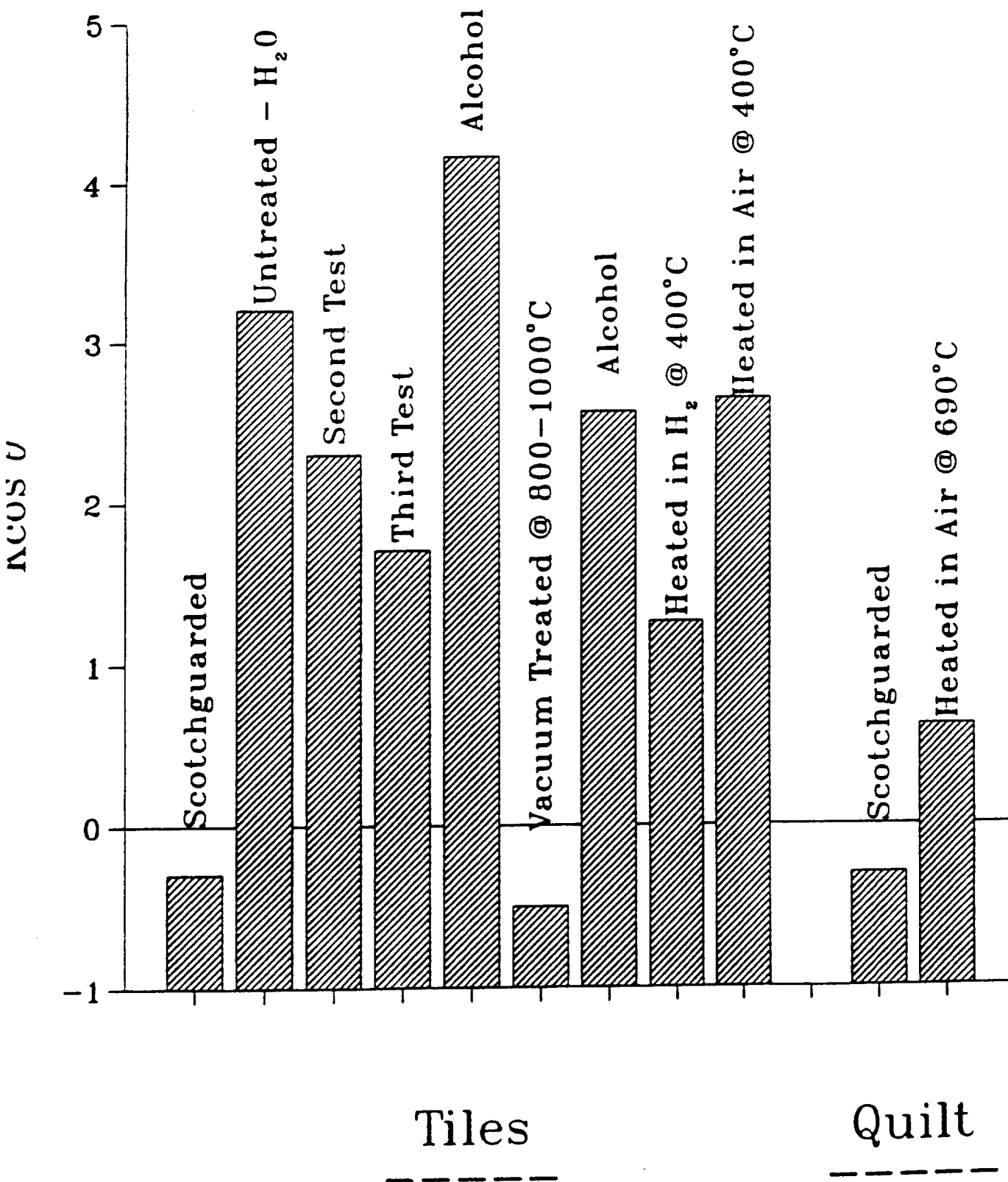
Fig. 7 Illustration of effect of Space Shuttle tile sample history on contact angle.
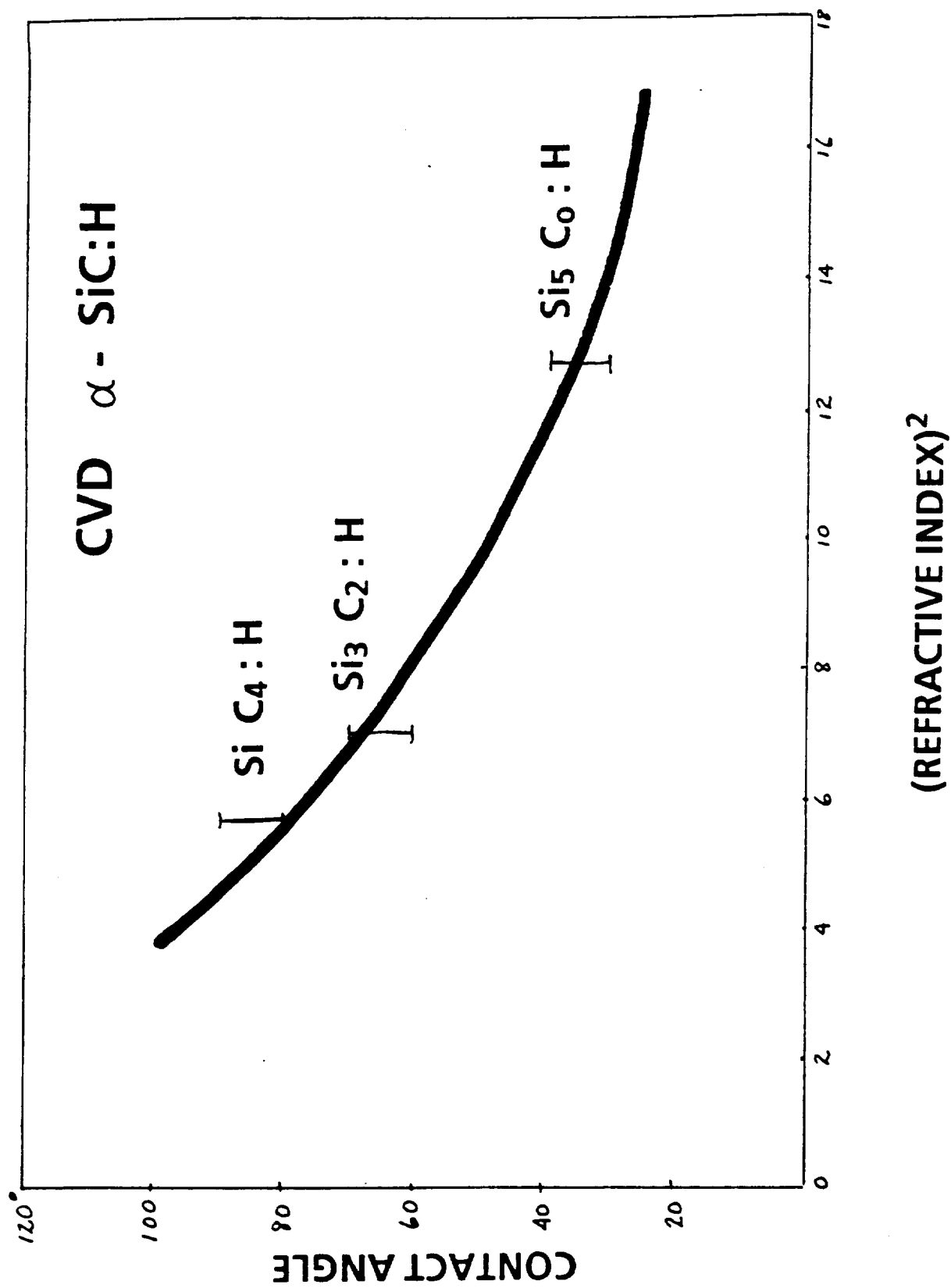
Fig. 8   Rotation between contact angle and refractive index.
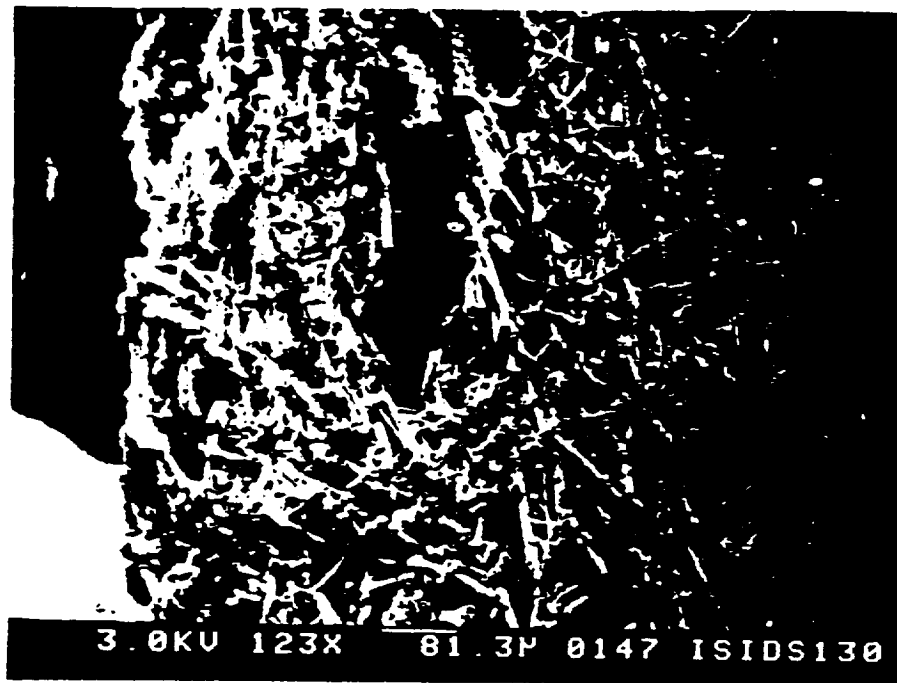
Fig. 9 Scanning electron micrographs of Amercom CVD SiC coating on L1-900.
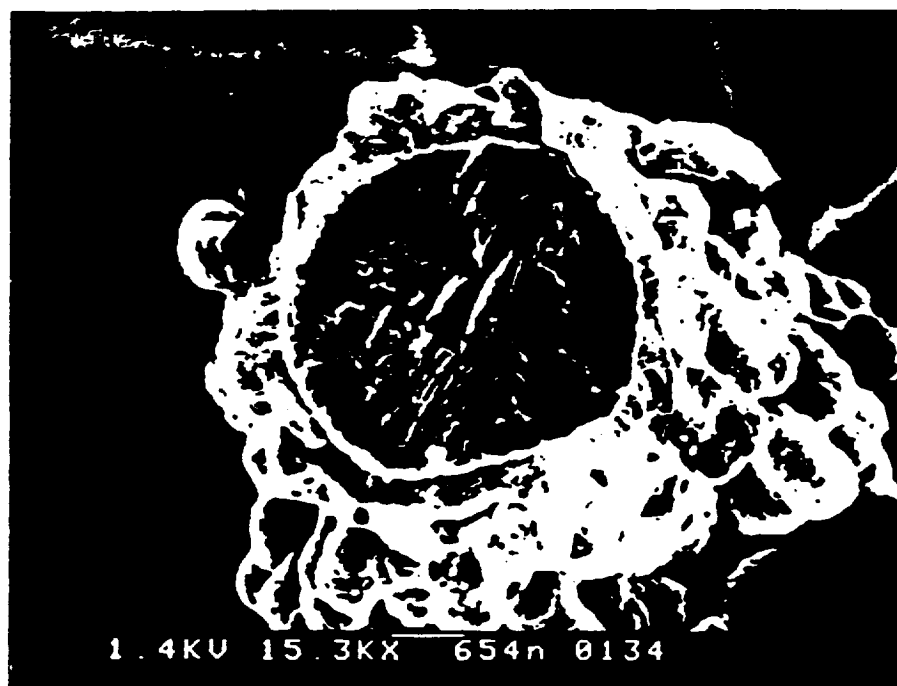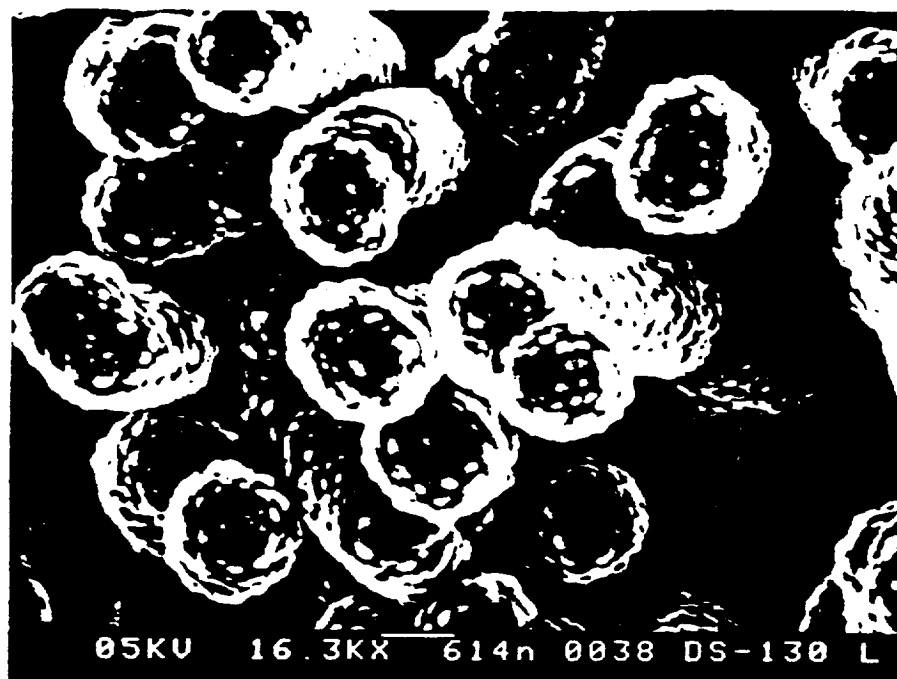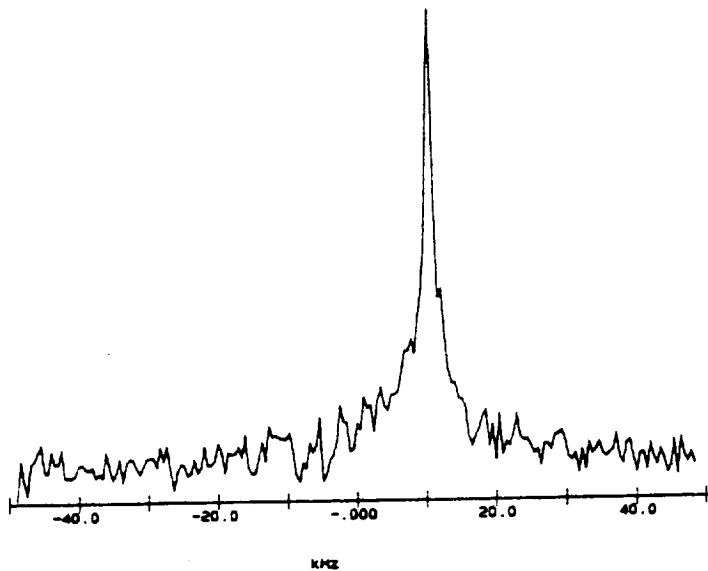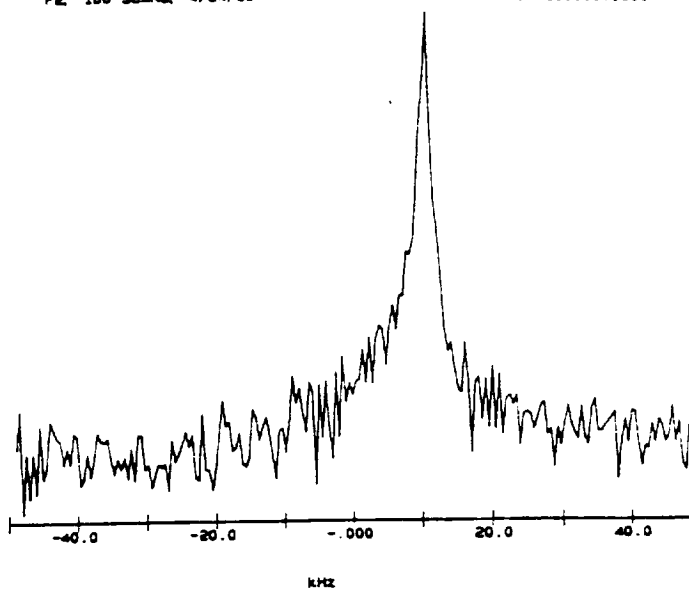
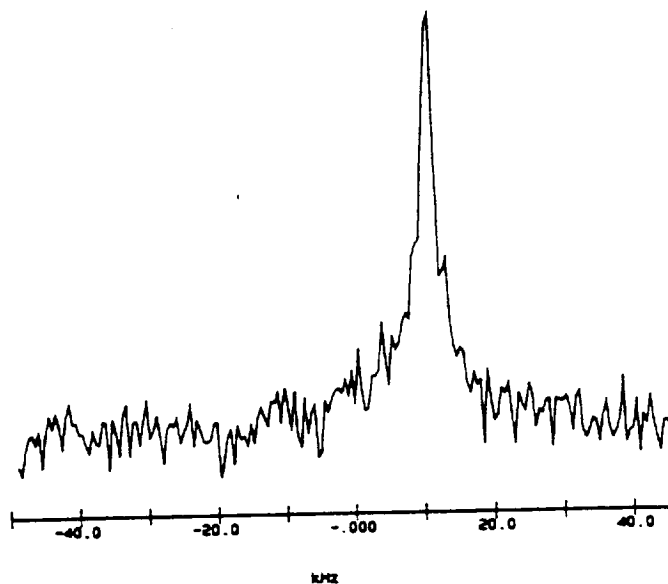Fig. 10 Scanning electron micrographs of Amercom CVD SiC coating on L1-900.
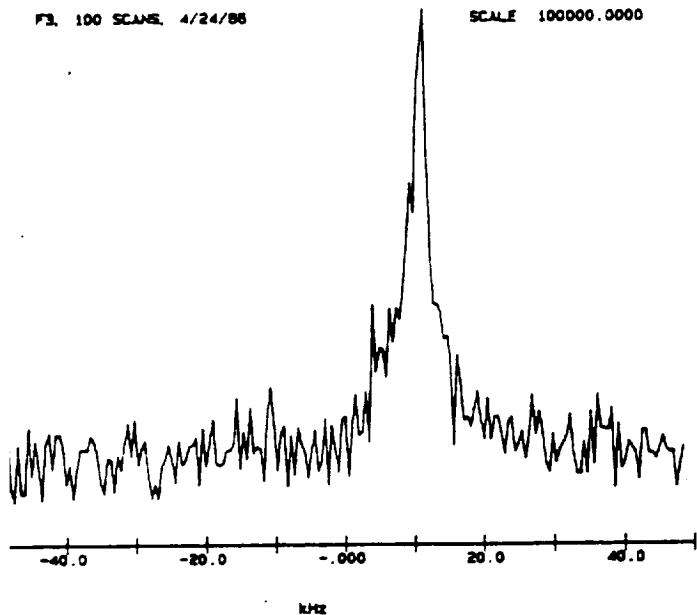
Fig. 11 NMR spectra of Space Shuttle tile samples;
F1, as received
F2, 1st vacuum treatment
F3, 2nd vacuum treatment
F4, after three soakings

APPENDIX I

WATER ABSORPTION

IN THE

SPACE SHUTTLE TILES

Laura Powers
MSE 130
Professor R. M. Fisher
May 20, 1985

Summary

The ceramic insulating tiles that protect the Space Shuttle Orbiter from extreme launch and re-entry temperatures have been subjected to various water absorption tests as well as being characterized by scanning electron microscopy (SEM) and BET surface area analysis. Measurements of the amount and rate of water absorption have confirmed the extreme hygroscopic behavior of the tiles, which are approximately 93% void and composed of high purity amorphous silica fibers.

Experiments have shown that an unwaterproofed tile will act virtually as a sponge, soaking up about six times its weight in water. Small samples of both unwaterproofed and waterproofed tile were immersed in water and allowed to air-dry, with five faces exposed to the atmosphere. The waterproofed samples (coated with Scotchguard) absorbed varying degrees of water, indicating a dependence on coating coverage and uniformity. The evaporation time for unwaterproofed tiles indicated that a period of at least two to three days was necessary for full evaporation of retained water.

Water absorption in the tiles has been modeled by a modification of the capillary rise of liquids, and experiments have shown good agreement with theory; experiments simulating capillary action of water around silica-based glass have yielded contact angle measurements ($17° \leq \theta \leq 26°$) close to the known value of $\theta = 18°$. Scotchguard-coated glass showed no water absorption by capillary action, corresponding to a contact angle of $180°$. Interestingly, though, experiments simulating partial Scotchguard coverage showed a relatively large amount of absorption.

Finally, a few basic characterizations of the tiles have been made. Scanning electron micrographs revealed an interesting web-like coverage of Scotchguard on the fibers. Also, micrographs of Scotchguard on a flat metal surface verified the particulate nature of the substance and indicated that the Scotchguard particles agglomerate as more is applied. BET surface area analysis was also performed on a slightly-ground sample, yielding a specific surface area of 0.704 ± 0.017 m^2/gm, which is within the calculated, theoretical range. However, there were several difficulties involved with this measurement, since the area is so small (< 1 m^2/gm).

These experiments were performed as a preliminary investigation into methods of possibly reducing the water intake by the tiles at cracks and gouges in the waterproof glass coating (the RCG). Since part of the Scotchguard coating burns off during re-entry (at any isotherm $>1000°F$ in the tile), and is also known to weaken the bonding adhesive in the tile system, further investigation into more durable waterproofing materials is certainly meritable. An alternative to reduce water pick-up is to modify the pore structure of the tiles on the upper surface, beneath the RCG coating.

Appendix II

Program Summary Prepared For
Howard Goldstein - Branch Chief
Thermal Protection System Materials
NASA-Ames Research Laboratory

WATER ABSORPTION BY SPACE SHUTTLE TPS MATERIALS[**]

OBJECTIVES AND PRINCIPAL RESULTS

* **TO UNDERSTAND THE EXTREME HYGROSCOPICITY OF SPACE SHUTTLE TILES**
  (untreated samples rapidly absorb 6 times their weight of water)

    **Pronounced Hydrophilic Nature Of Fused Silica Fibers Is Due To
    Silonal (SiOH) Groups On The Surface**

    Contact angles of fibers in heat shield materials determined by
    quantitative measurements of rate of capillary rise and application
    of the Washburn equation.

    Contact angles of 5 - 10 degrees (similar to highly wetting fused
    silica and glass) observed on uncoated samples.

    Contact angles > 90 degrees on samples treated with Scotchguard.

    Removal of hydroxyls (OH) by vacuum drying (>800 $^{\circ}$C) produces a
    hydrophobic surface.

    Hydrophobicity lost by heating in air or tank hydrogen (>400 $^{\circ}$C)
    or rinsing with acid or alcohol.

    NMR measurements suggest that several water layers are attached to
    surface hydroxyls after tiles are saturated with water.

    NMR measurements should be extended and supplemented with FTIR,
    SIMS and other analyses of as-produced and thermally- or chemically-
    treated fibers to develop aquantitative picture of internal and
    surface structures. (Prior removal of surface hydroxyls may be
    necessary to achieve good adherence of hydrophobic coatings)

** NAS-2-A28207C

Principal Investigator - Robert M. Fisher, Lawrence Berkeley Laboratory
                                             Univ. of California, Berkeley.
Technical Monitor   - Robert L. Altman, Thermal Protection Materials
                                             NASA Ames Res. Center.

* **TO EXPLORE NOVEL METHODS OF PRODUCING INORGANIC HYDROPHOBIC SURFACES**
  (fluorocarbon waterproofing agents burn off during re-entry)
  (process must infiltrate heat shielding to coat all fibers)

  Application Of CVD Coatings To Produce Hydrophobic Surfaces

  Wettability Of Candidate Coating Materials Determined

  Contact angles of potential coatings deposited on glass or aluminium
  and flat samples of reference materials measured using the tilting
  table method.

  Contact angles of metal oxides are too low to be water repellent.

  CVD films of amorphous "TiN" or "SiC:H" on glass are non-wetting.

  SiC:H remains hydrophobic after heating to 400 C whereas TiN or
  bulk SiC do not.

  Preliminary attempts to apply a subsurface CVD coating to fibers
  were not successful.

  Further work is necessary to establish feasibility of CVD coating
  fibers within a tile and the optimum surface for good adherence.

  Other New Approaches To Waterproofing

  Infiltrating tiles with sol-gel or other solutions to deposit
  compounds resistant to hydroxyl formation may reduce hygroscopicity.

* **TO IDENTIFY METHODS OF MEASURING MOISTURE CONTENT OF HEAT SHIELDING**
  (for possible field inspection of the Space Shuttle)

  NMR Instrumentation Could Be Used For Field Inspection Of Wet Tiles

  Specific design criteria could be developed.

APPENDIX III

SYMPOSIUM L

MATERIALS FOR AEROSPACE APPLICATIONS

APRIL 23-24, 1987

Chairs

A. Madhukar
University of Southern California
Los Angeles

L. Leger
NASA Johnson Space Center
Houston

Co-Sponsor

MRS-Southern California Chapter

L3.5

FACTORS AFFECTING WATER ABSORPTION BY SPACE SHUTTLE TILES.
Robert M. Fisher and Patrick Dalton, Center For Advanced Materials,
Lawrence Berkeley Laboratory, University of California, Berkeley, CA
94720; and Robert L. Altman, Thermal Protection Materials Office,
NASA-AMES Research Center, Moffett Field, CA 94035.

Because of the hydrophilic nature of untreated silica fibers, Space
Shuttle thermal protection tiles can absorb more than 6 times their
own weight of water. Waterproofing with fluorocarbons is quite
effective but the availability of water-repellant coatings with
greater thermal stabilty is desired. The factors that effect water
absorption have been examined by capillarly rise rate measurements and
application of the Washburn equation to obtain the apparent contact
angles with water after various treatments. Preliminary NMR
measurements of hydroxyl content before and after heating in vacuum
and other treatments have been obtained and the contact angles and
thermal stability of various plasma-activated CVD coatings evaluated.

Amorphous CVD films of SiC:H on glass with Si/C < 3/2 are non-wetting
and stable to heating in air to 400 Celsius whereas "TiN" and other
films and bulk SiC are not.

APPENDIX IV

ELECTRON OPTICAL CHARACTERIZATION OF AMORPHOUS SIC:H CVD FILMS

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* Center For Advanced Materials, Lawrence Berkeley Lab., Univ. of Cal.
** National Center for Electron Microscopy, LBL, Univ. of California
*** Univ. of Washington, Seattle, WA 98195
**** Dept. of Chem. Eng., Univ. of California, Berkeley Ca., 94720.

ABSTRACT

The utility of various electron optical methods to characterize the microstructure and composition of thin films of amorphous silicon-carbon films formed by plasma-activated CVD of SiH_4 and CH_4 has been investigated. The techniques employed include conventional and high resolution transmission electron microscopy and diffraction, non-dispersive x-ray spectroscopy and electron energy loss spectroscopy.

INTRODUCTION

The unique properties of amorphous hydrogenated silicon-carbon alloys make them candidates for a wide variety of applications for advanced materials. They have been studied for possible use as a wide band-gap semiconductor for multilayer solar cells [1], as a visible-light emmitting device [2], and for very hard, thin-film coatings [3]. The large number of new publications on this subject promises that other applications for these materials will surely be discovered in the future (e.g. MRS 1986 Spring Meeting, Palo Alto).

To understand their properties and to explain the effects of the many processing variables it is necessary to gain deeper knowledge of the complex relationships among microstructure, atomic structure, deposition conditions, and mechanical and electronic properties. As a first step toward this goal, we have evaluated the applicability of some of the electron optical tools that are available to characterize microstructures and chemical composition with reference to the influence of deposition conditions on plasma-activated CVD films of amorphous hydrogenated silicon-carbon alloys.

EXPERIMENTAL METHODS

The following conditions for plasma-activated CVD of α-SiC:H films were employed. The pressure in the reaction chamber was maintained at 300 mtorr with a total gas flow rate of 100 sccm. The $SiH_4 + CH_4$ content of the gas stream totalled 5% and He was used as a dilutent at 95% concentration. The power density of the plasma was maintained at 0.08 Watts/cm^2. The CVD films, from 50nm to 1100nm in thickness, were formed on either Al foil (or Al evaporated on glass), glass, quartz or evaporated carbon films mounted on electron microscope grids. The usual substrate temperature was 275 °C although in some cases the substrates were not heated and remained close to room temperature.

CVD films of SiC:H on carbon films were examined directly in the electron microscope. Films deposited on Al foil were stripped from the substrate by dissolving the Al in HCl and capturing small pieces on 200 mesh electron microscope Cu grids. Mounted specimens were rinsed in a methyl alchohol-water solution. SiC:H specimens were examined in a JEOL 200CX transmission electron microscope (TEM) or in a Philips 400 equipped with a Kevex energy dispersive x-ray spectrometer ((EDS) system and a Gatan Inc. electron energy loss spectrometer (EELS).

ELECTRON MICROSCOPY

The microstructure of a CVD film of Si:H, i.e. contains no carbon, deposited
on Al foil to a thickness of about 1 micrometer is illustrated in Fig. 1.
The columnar structure with hemispherical tops is quite apparent. The darker
lines that appear in the micrograph are roll markings on the surface of the
Al and it may be noted that the columnar structure is not influenced by this
or other structures on this scale. The films are surprisingly clean except
for occasional aluminum oxide particles that adhere to the film.

Fig. 1) TEM of a thick (1um) CVD film of Si:H deposited on Al foil.
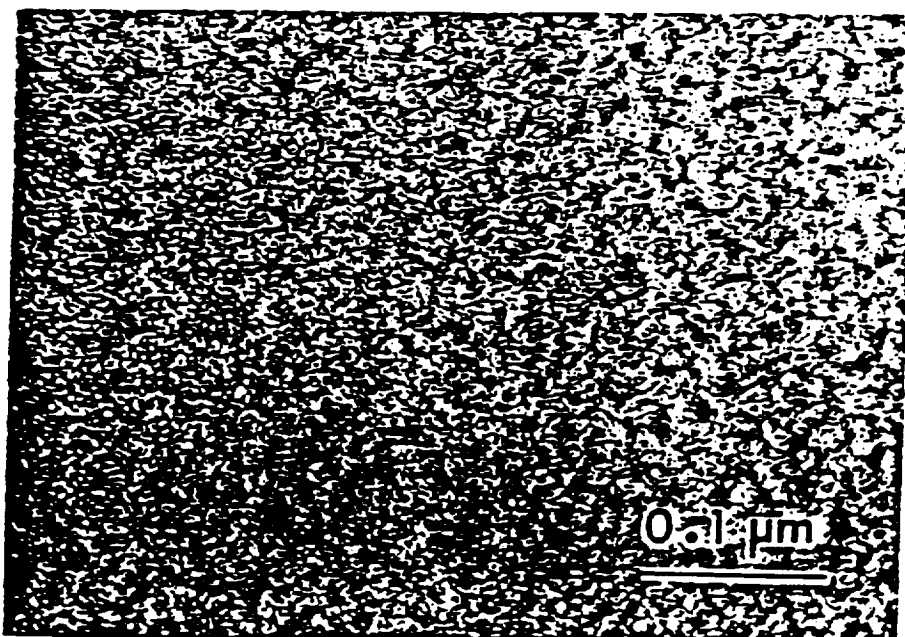
Fig. 2) TEM of a thin film (100 nm) of $Si_{0.65}C_{0.35}$:H CVD on carbon.

The apparent tendancy for CVD films with Si/C around 1.5 and deposited on evaporated carbon to separate into 2 "phases", as illustrated in Figure 2, is under further study. High resolution TEM revealed the presence of small particles from 5 to 50 nm in diameter. Electron diffraction analysis of the larger particles showed that they were crystalline graphite. Lattice images and optical diffraction of the very small particles suggested that the small particles are also graphite although the identification was not definitive.
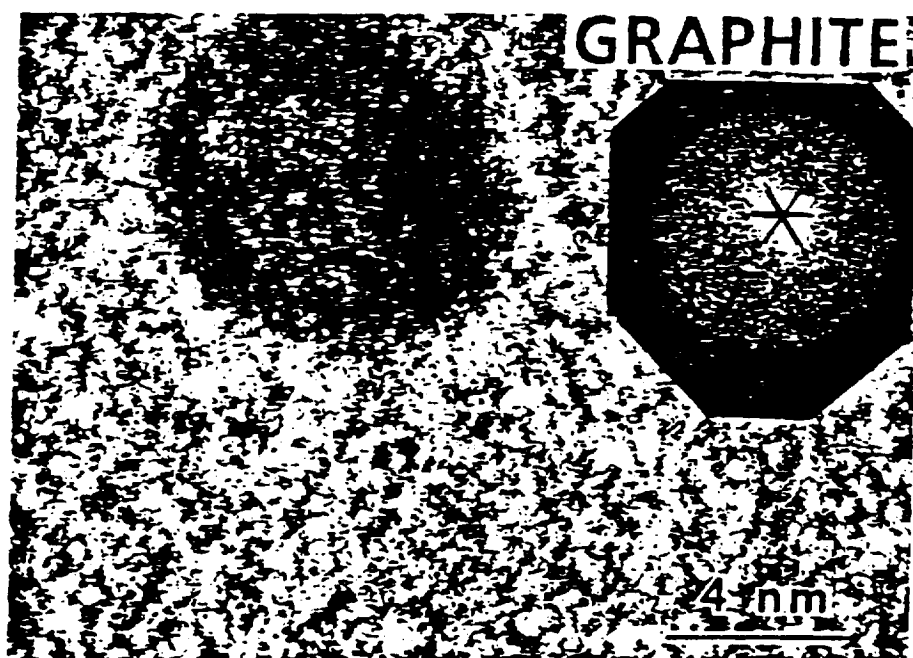
Figure 3. TEM of SiC:H film CVD on an evaporated carbon substrate.
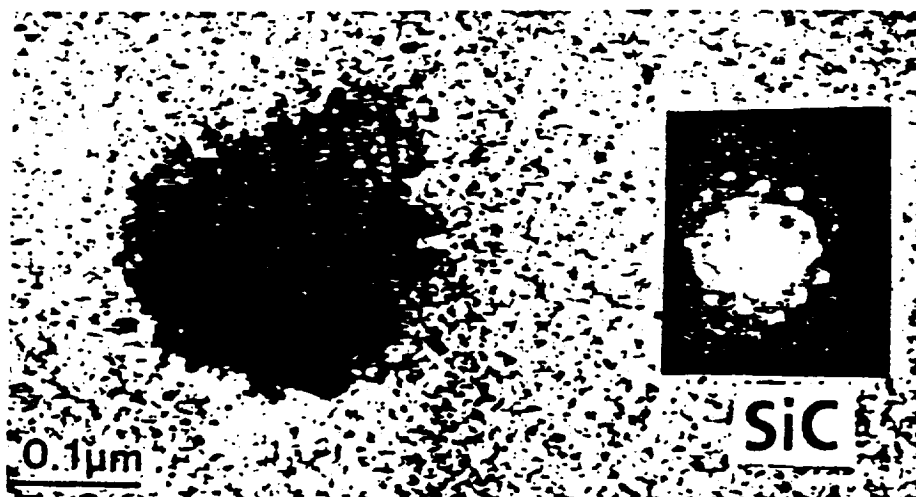
Fig. 4) CVD $Si_{0.65}C_{0.35}$:H showing beam-induced SiC crystallization.

The higher beam intensity used in the TEM-STEM mode for EDS and EELS analyes resulted in the crystallization of CVD films with Si/C near 1.

ENERGY DISPERSIVE X-RAY SPECTROSCOPY

EDS was used to confirm that the films stripped clean from the Al substrate. The occasional particles found on the films were readily identified as Al oxide. The carbon content is measurable with a thin window detector and such measurements will be carried out for comparison with EELS analysis.

ELECTRON ENERGY LOSS SPECTROSCOPY

During transmission through a thin foil specimen some or all of the electrons in the beam undergo inelastic scattering and transfer energy to the sample by exciting atomic and lattice transitions [4]. These energy losses can be detected with a magnetic prism spectrometer and can be used to identify the atomic species present in the sample and their concentration by the location and magnitude of K, L and M edges. Information about specimen thickness and other parameters can be derived from observations and measurements of the low-loss (5-100 ev) portion of the spectrum. The results of such measurements are illustrated in this section.

Fig. 5a shows the EELS for a CVD sample with a Si/C of about 1.4. The spectrum covers the range from 0 to about 500 ev. The scale is changed by a factor of 400 at 50 ev to reveal the C K edge. The Si K edge of this sample is shown in Fig. 5b.

The 0 and low loss region is shown with an expanded scale in Fig. 5c. The occurance of 1 strong plasmon peak indicates that the specimen is about 160 nm in thickness. Plasmon peaks are quite sensitive to electron density and related factors. Changes due to H content of the samples were noted and will be reported separately.

Fig. 5) EELS spectra of CVD SiC.

The total amount of inelastic scattering, I_{in}. (integrated from 0 to max. loss, usually taken to 1000 ev as contribution beyond this level is very small) depends on the scattering cross (atomic number and density) and the sample thickness. Apparent scattering cross sections depend on instrument parameters so that it is preferable to run a sample of known thickness to check the calibration. Results of measurements of total inelastic scattering are shown in Fig. 6.
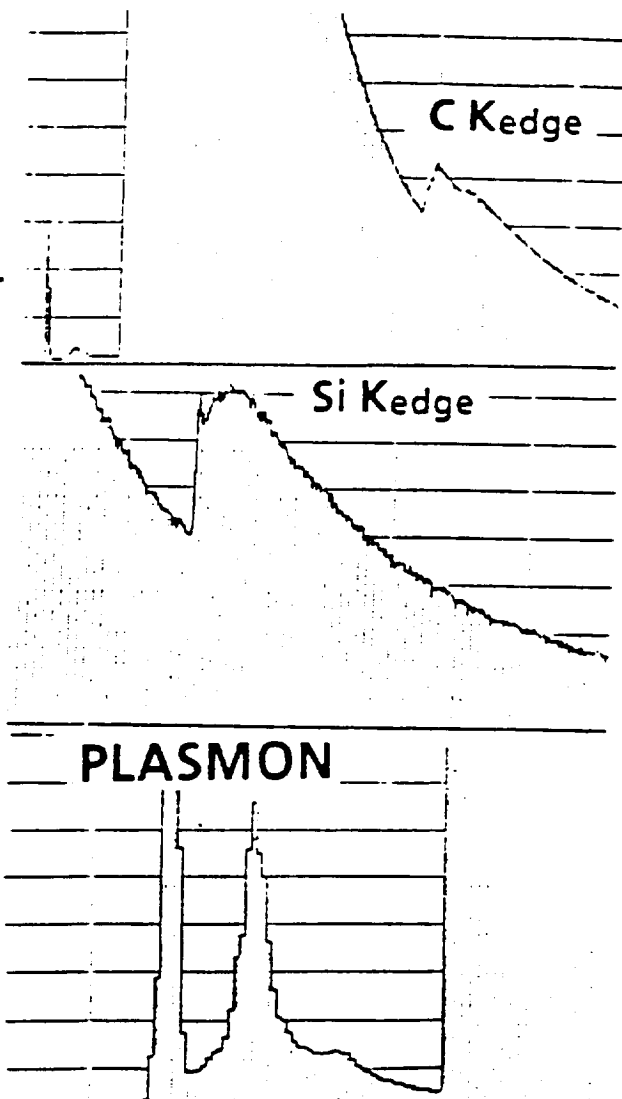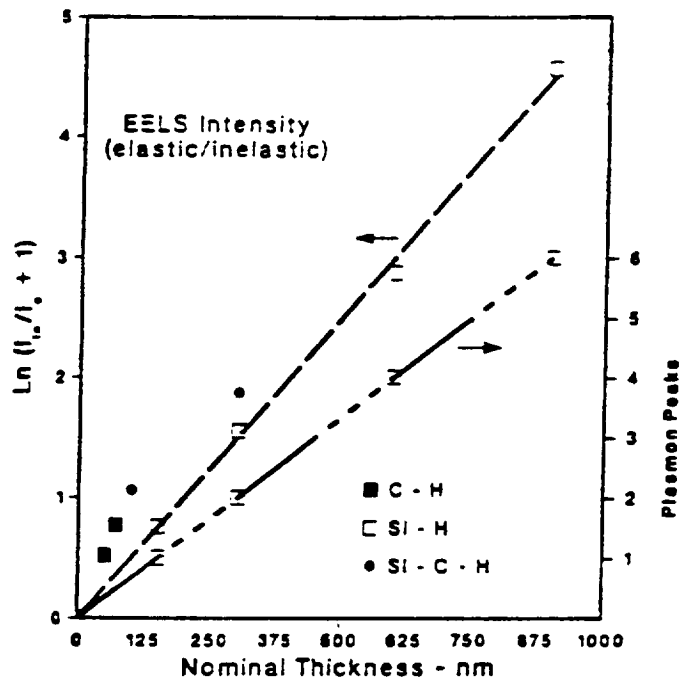
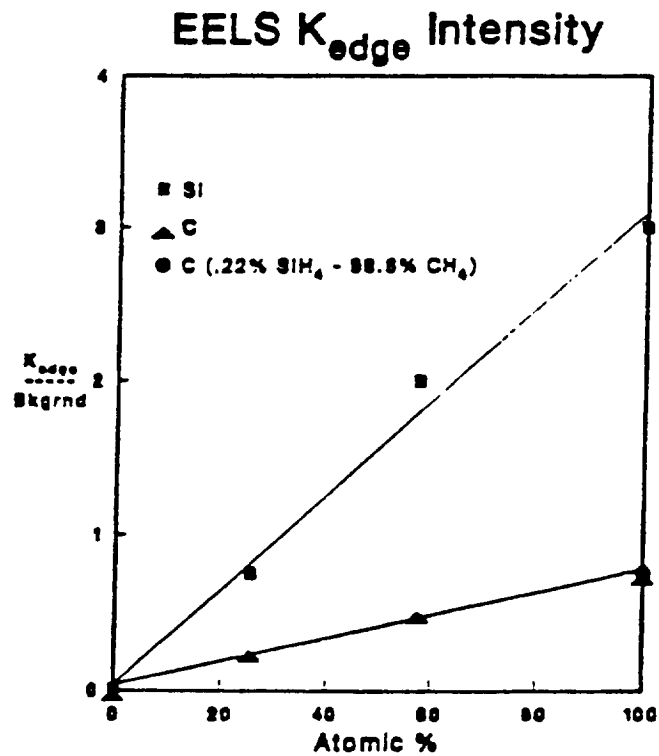Fig. 6) Effect of thickness on plasmon spectra and inelastic scattering.

Fig. 7) Effect of composition on Si and C k edge intensity.

As illustrated in Fig. 7, EELS can be used to obtain a qualitative measure of the composition of thin films. A comparison of Rutherford Back Scattering measurements and EELS data on companion samples is shown in Fig. 8. The agreement between the two methods is quite good.
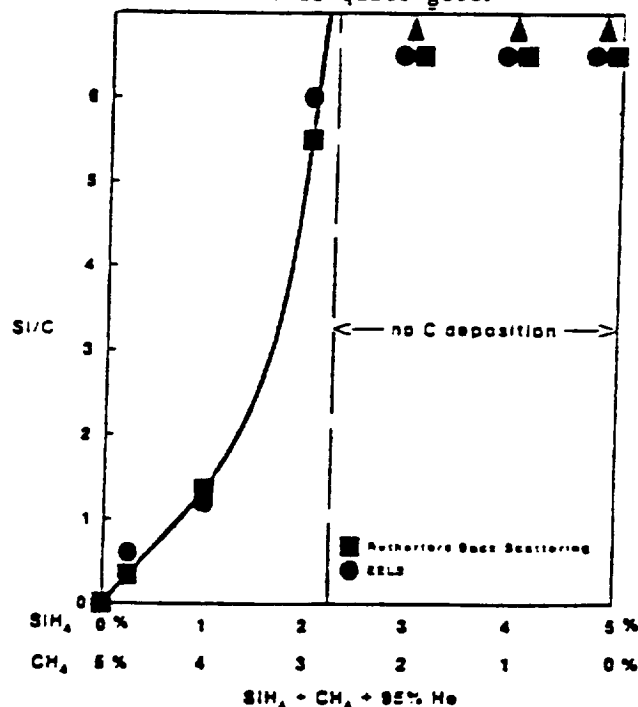
DISCUSSION

This preliminary study of CVD films of SiC:H has demonstrated that analytical electron microscopy can provide a great deal of information about their thickness and composition and their stability under the beam. TEM and electron diffraction indicate that the samples are amorphous but atomic-level microscopy and image simulation will be necessary to establish a more specific structural model for these materials. As for chemical analysis the EELS technique has the advantage that it can be used in the course of electron microscope and electron diffraction studies of the microstructure of CVD thin films without recourse to other instruments. The relationships between microstructure as determined in this study and electronic properties will be reported separately.

REFERENCES

[1] Y. Tawada, H. Okamoto, Y.Hamakawa, Appl. Phys. Lett. V39(3), 237 (1981)
[2] H. Munekata & H. Kukimoto, Appl. Phys. Lett. V42(5), 432 (1983).
[3] M.A. Bayne, Z. Kurokawa, N.U.Okorie, B.D. Roe, L. Johnson,R.W.Moss, Thin Solid Films V107, 201 (1983).
[4] N. Zaluzec, Bulletin of the Electron Microscope Society of America, V15, (1985) 72.

ACKNOWLEDGEMENTS

APPENDIX V

Relation of the Contact Angles of Materials
to their Dielectric Constants

Discussion

The contact angles of materials with water, reflecting their
hydrophobic-hydrophilic character, are commonly considered in terms of
the net change in surface energy when an element of surface is covered
with water or some other liquid of interest. This approach leads
directly to the classical Young equation illustrated in Figure 12,
where the relevant surface energies are for the vapour-liquid,
solid-vapour, and solid-liquid interfaces respectively.

The usefulness of this relation for predicting contact angles,
and hence wettability, is limited by much uncertainty regarding the
solid-liquid interfacial energy and in many cases its value can only be
derived from experimental observations of the contact angle of the
particular system in question.

One major source of difficulty when attempting to estimate
contact angles from knowledge available from another system, is the
possible occurance of a chemical reaction between solid and liquid.
The formation of an intermetallic compound or dissolution of the solid
when exposed to a molten liquid can contribute a very large term to the
energy balance. Trace elements in the melt may also react with the
surface to form an oxide layer. These effects and the related reaction
kinetics can severely confound direct interpretation of the apparent
contact angle and especially efforts to predict the wetting behavior in
other circumstances.

Less obvious surface reactions can also occur and affect
wetting behaviour. Perhaps the best known case is the hydroxyllation
of the surface of silica by water. The resulting Si:OH silanol groups
are a distinct surface phase that readily bond with water molecules and
so have a profound effect on wetting and contact angles.

* The apparent correlation of contact angle with the dielectric
constant of the substrate was discovered after completion of the
NASA-funded study at the Center for Advanced Materials, Lawrence
Berkeley Laboratory.

An even more subtle surface reaction is Van der Waals-like binding of polarizable molecules to a polarizable surface (2). The wetting of a clean gold surface by water, where no chemical reaction should occur, is an important example of this effect (early observations of hydrophobic gold were a result of unrecognized contamination from organics, i.e. grease in the atmosphere).

If one component is already polarized, e.g. fluorocarbon molecules, repulsive forces will result in a higher energy state, non-wetting and a high contact angle. These considerations have lead the author to note a simple but useful correlation between contact angle and the dielectric constant of the substrate. Since the dielectric constant indicates the polarizability of a material, a close connection with the extent of its bonding with water molecules is to be expected. A paper by Stoneham and Tasker that deals in part with this connection has just come to my attention (3).

Handbook data on contact angles and dielectric constant for various materials as well as some results of recent measurements are plotted in Figures A5-1, A5-2 and A5-3, a surprisingly good correlation over a wide range of values is evident.

At first sight glass and silica would seem to be significant departures from the trend. However, when the surface silonals have been removed by vacuum treatment, the contact angle with water is in keeping with the bulk dielectric constant of silica (4). Thus, it is the polarizability or the dielectric constant of the surface that determines its contact angle. Infra-red techniques can be used to determine the refractive index of the surface and the corresponding dielectric constant.

A somewhat similar plot of the contact angle of SiC:H films against refractive index is shown in Fig. A5-2.

A more detailed discussion of this correlation in terms of the Van der Walls formulation will be presented in an expanded version of this working paper (1). Even in this general graphical form, the simple conceptual approach to the choice of surface coatings to attain good water repellent characteristics is extremely useful.

(1) A.P. Tomsia and J.A. Pask, "Chemical Reactions and Adherence at Glass/Metal Interfaces: An Analysis," Dental Materials, Vol. II, 10 (1986).

(2) Anthony W. Adamson, "Physical Chemistry of Surfaces," Wiley Interscience, 1985.

(3) A.M. Stoneham and P.W. Tasker, "Metal-Non-Metal and Other Inferfaces: The Role of Image Interactions," J. Phys. C: Solid State Phys. 18, L543 (1985).

(4) R.M. Fisher, P. Dalton and R.L. Altman, "Water Absorption by Space Shuttle Tiles," presented at the Materials Research Society, Anaheim, California, April 21-15, 1987.

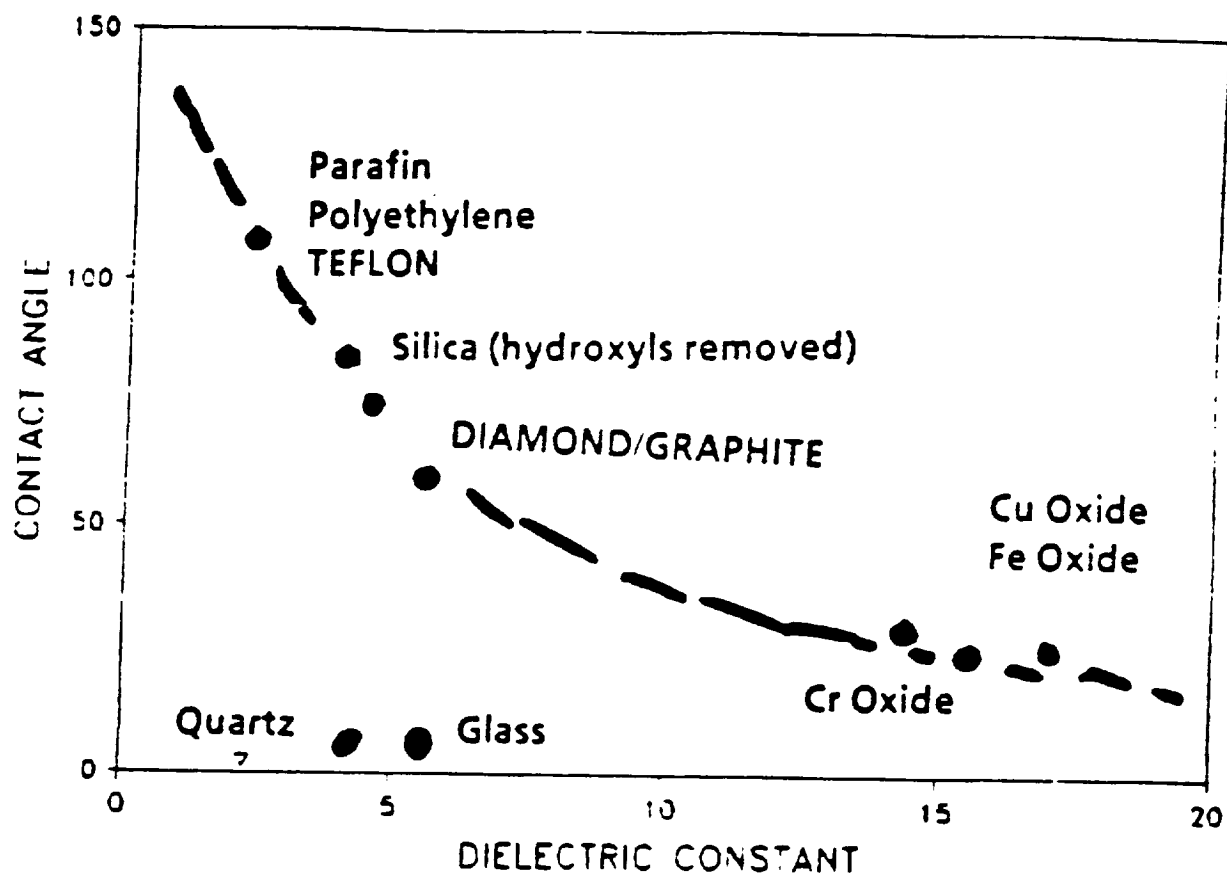# CONTACT ANGLE VS DIELECTRIC CONSTANT

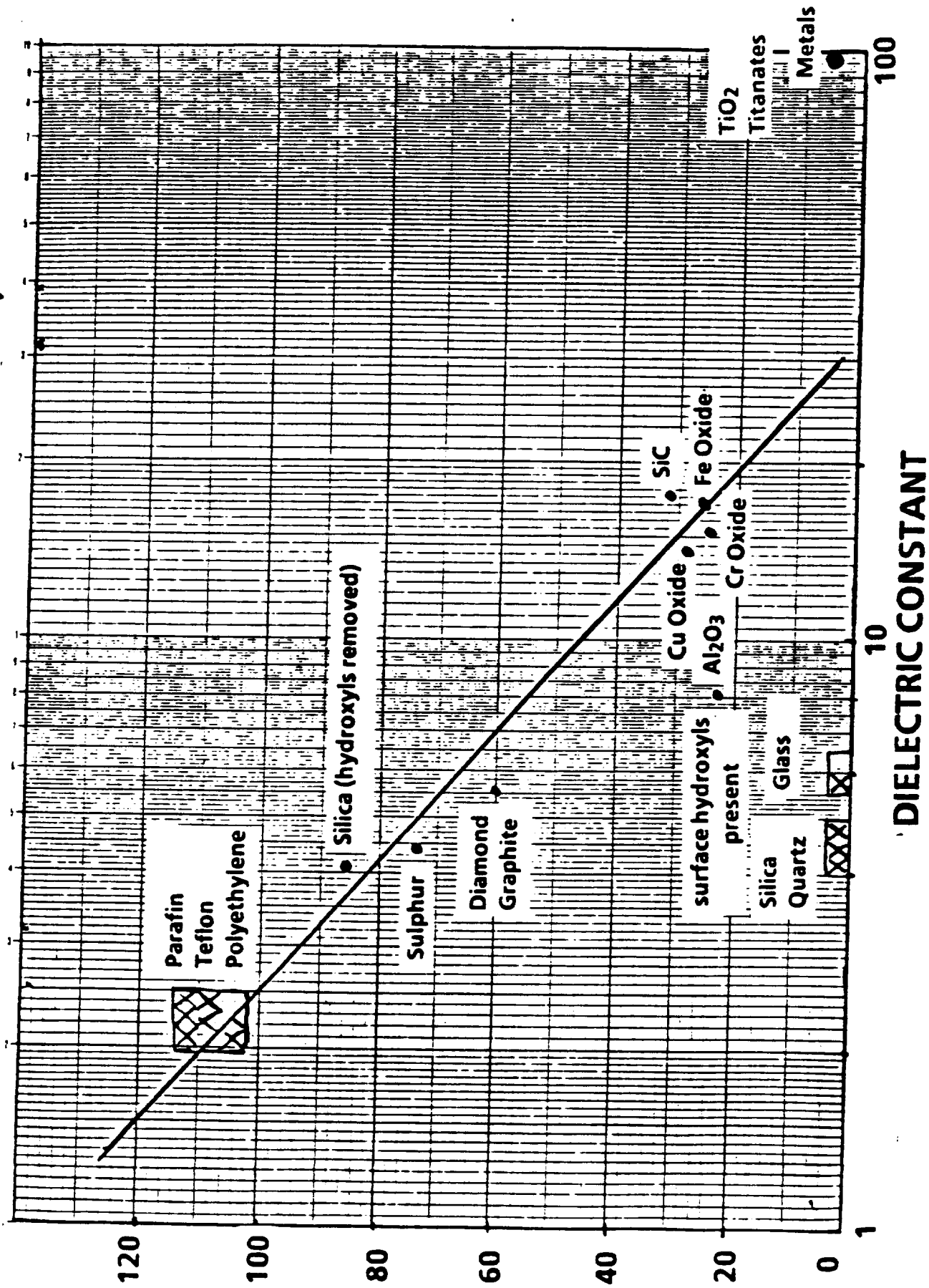Fig. A5-1 Relation between dielectric constant and contact angle.

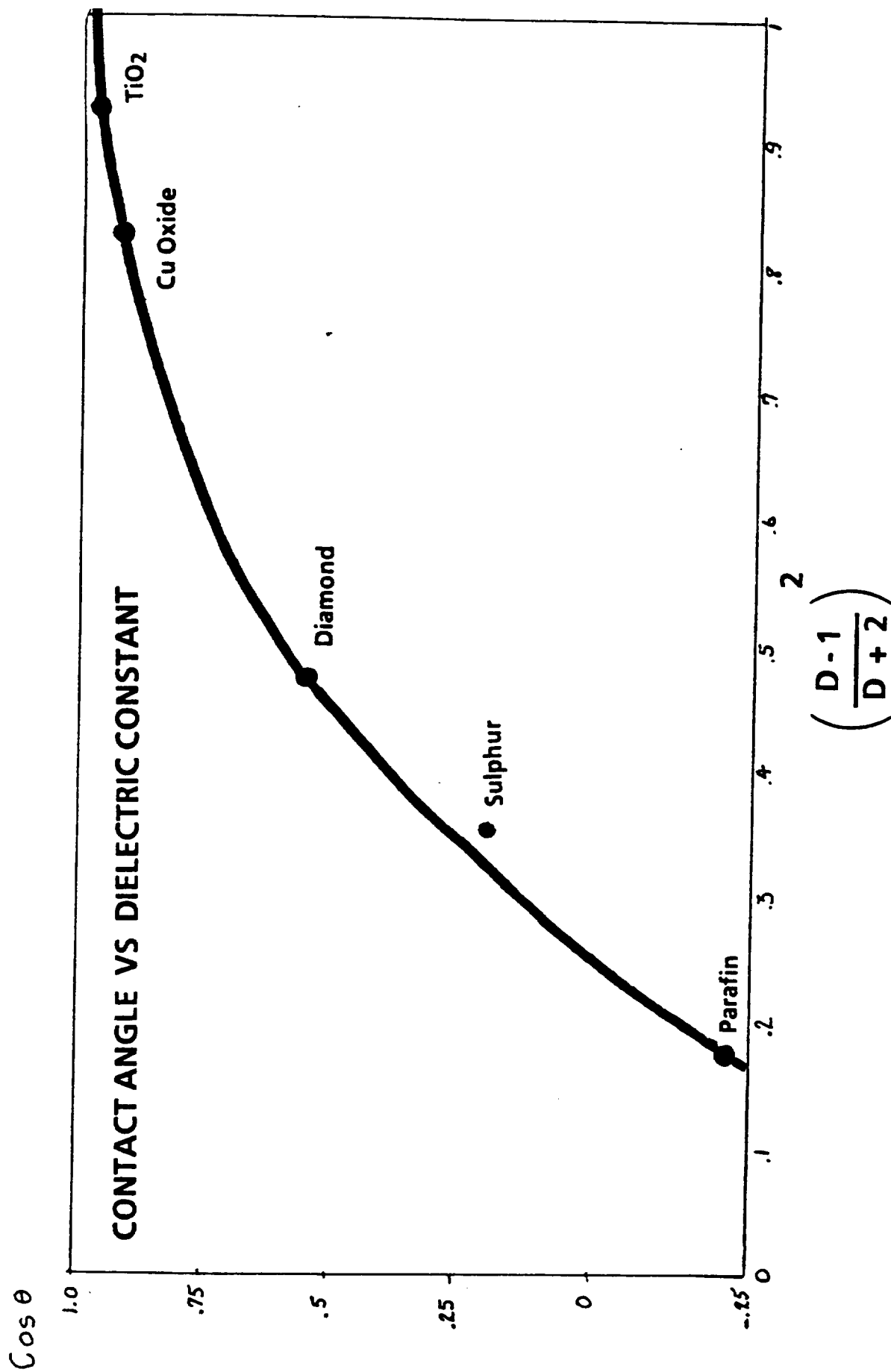Fig. A5-2 Relation between dielectric constant and contact angle.

Fig. A5-3 Relation between dielectric constant and contact angle.